Grain Refinement in Aluminum Alloyed with Titanium and Boron

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The aluminum corner of the ternary Al-B-Ti diagram was explored. A eutectic: Liq → Al
+ TiAl₃ + (Al, Ti)B₂ was found at approximately 0.05 wt pct Ti, 0.01 wt pct B; 659.5°C. TiB₂ and
AlB₂ form a continuous series of solid solutions, but no distinct ternary phase was found. The
addition of boron to aluminum-titanium alloys expands the field of primary crystallization of
TiAl₃ toward lower titanium contents and steepens the liquidus. In equilibrium conditions, pro-
nounced grain refinement is found only in alloys in which TiAl₃ is primary and nucleates the
aluminum solid solution before any other impurity can act. The peritectic reaction facilitates
this priority but it is not necessary for grain refinement. Because of the low diffusivity of ti-
tanium and boron in aluminum, equilibrium is seldom attained and in commercial practice grain
refinement by TiAl₃ is found also outside its equilibrium field of primary crystallization.

IT is well known that additions of Ti, Zr, V, and so
forth produce grain refinement in aluminum alloys. It
is also well established that additions of boron to ti-
tanium-bearing alloys enhance the grain refinement.
Two main theories have been advanced to explain these
phenomena:
1) The carbide (or boride) theory.
2) The peritectic reaction theory.
Cibula[1] has shown that when carbides of V, Ti, Zr,
and so forth, and borides of aluminum and titanium are
present in aluminum alloys, pronounced grain refine-
ment is produced through nucleation. The main argu-
ments for the nucleation being due to the carbides or
borides are:
1) The carbides and borides are very stable (have
very high melting points).
2) The atomic spacing in the close packed planes of
the carbide and the boride are only a few percent dif-
ferent from the corresponding spacing in aluminum.
Crossley and Mondolfo[2] have shown that pronounced
grain refinement could be obtained in alloys containing
primary crystals of TiAl₃, ZrAl₃, and other compounds
reacting peritectically with aluminum, but not with
FeAl₃ which forms a eutectic with aluminum. Crossley
and Mondolfo, Mascré et al.[3] and Nakao[4] show that
heavy carbon additions to aluminum-titanium alloys
reduce the grain refinement. Nishimura et al.[5] report
that the addition of TiC to aluminum does not refine
the grain, unless the melting is done in air. They
speculate that TiN is formed, which refines the grain,
but their evidence does not exclude the reaction of TiC
with oxygen to liberate some titanium which goes to
form TiAl₃. Seeman and Staats[6] report no grain re-
finement with additions of TiB₂ or VC, but refinement
with Ti, TiC, Ti + TiB₂. Moriceau[7] has shown micro-
probe photographs which he interprets as proving that
TiB₂ nucleates aluminum. However, the fact that in his
particles the boron-rich zone is decidedly smaller than
the titanium-rich one, could indicate that aluminum is
diffusing into the TiB₂ and titanium out of it so that the
actual particles consist of a core of (Al, Ti)B₂ sheathed

by TiAl₃. More recently, Davies et al.[8] show that there
is epitaxy between TiAl₃ and the aluminum, with the
TiAl₃ being found at the center of the aluminum crys-
tals, but no epitaxy between the diboride and the matrix,
with the diboride at the grain boundaries. They specu-
late that the effect of boron is to decrease the solubility
of titanium and thus increase the number and dispersion
of nucleating TiAl₃ particles.
The information on the equilibrium diagram is scanty.
The binary diagrams for aluminum-titanium and alumi-
num-boron are reasonably well established[9,10] but the
information on the aluminum-carbon system is not too
reliable. No information was found on the ternary
Al-C-Ti. On the Al-B-Ti diagram the only available
information is the report by Wheeler[11] of the existence
of a compound TiB₂Al₃.
In order to throw more light on the grain refinement
of aluminum alloys a series of experiments was started.
Three somewhat separate investigations were con-
ducted:
1) Nucleation of aluminum by intermetallic com-
pounds.
2) Exploration of the equilibrium diagrams Al-B-Ti
and Al-C-Ti.
3) Effect of boron on grain refinement of aluminum-
titanium alloys.
The work done on the nucleation of aluminum by in-
termetallic compounds was reported in a separate pa-
per.[12] The main conclusions of that work which are
pertinent to the present investigation are: TiAl₃, VAl₁₀,
CrAl₇, NiAl₃, and AlB₂ are all good nucleants for alu-
minum; for TiAl₃, ZrAl₃, and VAl₁₀ there is at least
one orientation relationship in which nucleation takes
place at 0°C. undercooling.
The work on the Al-Ti-B diagram and the effect of
boron on the grain refinement are covered here. Also
reported are the few data on the addition of C-Al-Ti
alloys that were obtained.

MATERIALS AND TECHNIQUE

For the equilibrium diagram work, high purity ma-
terials were used: refined aluminum (99.99 + pct),*

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*Unless otherwise specified, all percentages are by weight.

sponge titanium, (99.5 + pct) amorphous purified boron,

and pure TiB$_2$ crystals. For the work on the effect of boron on grain refinement both high purity materials and two commercial master alloys were used; one containing 5 pct Ti, 1 pct B, the other 3.1 pct B. Starting from the high purity materials, two master alloys were prepared; one containing 7 pct Ti, the other 3.5 pct B. After analysis, these two alloys were mixed with aluminum to prepare the various alloys. Approximately one-quarter of the alloys prepared were analyzed, and in all of them it was found that the difference between the calculated and the actual analysis was less than the error of analysis. Some alloys were also prepared by adding large quantities of TiB$_2$ to molten aluminum, but, although they were thoroughly stirred and held at 900°C. for several days, a very limited amount of boride was retained in the alloy.

In the melting and alloying operations, all the possible precautions were taken to avoid carbon absorption. All the equipment that came in contact with the metal was carbon free: Alundum crucibles, Alundum stirring rods, Alundum thermocouple protection tubes were used in the melting, and the casting was done into copper molds, coated with an alumina-sodium silicate wash. Before any determination was conducted, the alloys made from the mixtures of master alloys and aluminum were either cycled several times up and down from 900°C to the freezing point, with frequent stirring, or held at 900°C for several days under a NaCl-KCl flux cover, also with frequent stirring. These practices were designed to approach equilibrium, because preliminary experiments had shown that in the boron-rich alloys most boron was present as AlB$_{12}$, and it was hoped that in this way the reaction AlB$_{12}$ + Liq → AlB$_2$ could be completed. Unfortunately, this was not always the case and in some of the high alloy samples AlB$_{12}$ was still present. Samples for the liquid solubility of boron and titanium as a function of temperature were prepared by holding titanium and boron-rich melts at temperature, allowing them to settle for at least 1 hr and extracting the sample from the top of the liquid.

The alloys used for the determination of the fields of primary crystallization were cooled slowly (20° to 40°C per hr) to close to the freezing point and then poured in a cold copper mold. In this way, microexamination could easily distinguish between the large primary crystals and the fine secondary crystallization.

The nature and composition of the phases was determined on alloys slowly cooled from 1100°C at a rate of 10°C per hr with overnight holds at constant temperature. This cooling lasted 6 days, including 48 hr at 630°C to insure at least partial completion of peritectic reactions. After quenching from 630°C and microexamining, these alloys were dissolved in dilute hydrochloric acid and the crystals of intermetallic compounds were recovered by decantation. Generally, the extracted material was composed of a mixture of crystals: large square platelets of TiAl$_3$ and small flat hexagons of diboride.

In none of the titanium bearing alloys could any diboride crystals be found which were large enough for nucleation experiments by the small droplet method.[12] (There are two diborides present in the system, AlB$_2$ and TiB$_2$, with the same crystal structure and very similar lattice parameters. No distinction will be made at this stage and the designation (Al, Ti)B$_2$ will be used.)

Well-formed crystals of TiAl$_3$ were separated by hand from the mixtures and carefully cleaned of any attached residue. Several of these crystals were used for nucleation studies, others were powdered and used for diffraction patterns and chemical analysis. Attempts to separate the TiAl$_3$ and (Al, Ti)B$_2$ crystals by a sink-float method, using diiodomethane (density 3.3) as the liquid were unsuccessful. A separation by size was obtained by stirring the crystal mixture in water and pouring out the water after a few minutes settling. The material still in suspension was separated by centrifuging and examined microscopically and by X-ray diffraction. Neither method detected any TiAl$_3$ in this fraction, but neither method excludes the presence of up to 5 to 10 pct TiAl$_3$, mixed with the boride.

Most of the alloys prepared were microexamined both as-cast and after prolonged (up to 2000 hr) homogenization at 640° ± 10°C. Lattice parameter measurements were done on powder patterns using a 114 mm camera and copper radiation. The diffraction lines of crystals extracted from alloys containing both titanium and boron were not as sharp as those of crystals from binary alloys or from the purchased TiB$_2$, indicating some variation of composition and lattice parameter, either from crystal to crystal, or more probably within the crystals themselves. The lattice parameters were calculated using a computerized version of Cohen's Least Squares Method. This program utilizes a multiple regression and correlation analysis and calculates standard deviation for d spacings and lattice parameters. Atomic number and atomic weight corrections are also applied to the data which are then used to calculate the sample density.

The temperatures of final freezing were determined from cooling curves taken with a Leeds and Northrup Speedomax, calibrated before and after each determination by running a cooling curve of pure aluminum. The accuracy of the temperatures is better than 0.2°C. In the titanium-rich alloys no under-cooling of the final freezing was ever detected but in the boron-rich alloys undercoolings up to 4° to 5°C were found. No effort was made to determine the beginning of solidification, because either no sharp change of slope could be detected, or undercooling of the order of 10° to 30°C made the results unreliable. Location of the eutectic was estimated from the amounts of primary crystals present and from the length of the eutectic arrest. Grain size of each alloy prepared was determined by casting approximately 100 g of the alloy from 750° ± 10°C into an Alundum crucible preheated to approximately 100°C. This casting was sectioned in the middle, machined and macroetched with Tucker's reagent.

High purity graphite, hexachlorethane and TiC were used to prepare Al-C-Ti alloys, but with little success. No consistent mixing was obtained and all the additions tended to separate from the metal. Supersonic vibration to facilitate mixing was tried, but with little effect. Because of this inability to prepare alloys with consistent composition only very scattered results were obtained.

RESULTS AND DISCUSSION

1) Equilibrium Diagram Aluminum-Boron-Titanium

One of the most important features of this work was that equilibrium could not be obtained in the majority of cases. This was due to two characteristics of the

system: presence of peritectic reactions and extreme slowness of the diffusion of titanium and boron in aluminum. This lack of equilibrium must be kept in mind in the interpretation of the results, because in practically all cases, extrapolation of the experimental data is necessary to determine the equilibrium, and this may be a source of error.

In all the samples examined, either of the alloys themselves or of the extracted crystals, the only phases found were aluminum, $TiAl_3$, $(Al, Ti)B_2$ and occasionally AlB_{12}. No evidence whatever was seen of a distinct compound $TiAl_3B_2$. All the lines found in diffraction patterns fit the above crystals and no extra lines were left to account for the ternary $TiAl_3B_2$ compound. This is only negative evidence, but it would be too much of a coincidence that the ternary compound should have a crystal structure whose X-ray reflections all coincided with those of AlB_{12}, $TiAl_3$, and $(Al, Ti)B_2$. Thus, the existence of a compound with a different structure can be excluded.

The composition and structure of the extracted crystals and the composition of the alloys from which they were extracted is shown in Table I. In some cases it was found that the extracted crystals of boride contained more boron than could be accounted for by a diboride, and the X-ray patterns showed lines of AlB_{12}. Calculations were made assuming that all the excess boron was present as AlB_{12} and that the remaining aluminum was present as $(Al, Ti)B_2$. The lattice parameters of these diborides fell in line with the other data indicating that the assumption was reasonably correct.

The first three samples in the table are tetragonal crystals of $TiAl_3$. As the table shows, only a small amount of boron can dissolve in $TiAl_3$, and this produces a small change in lattice parameter. For the boride crystals the atomic percent of boron is within experimental error of the theoretical, indicating an atom by atom substitution of titanium by aluminum.

The last six columns show a comparison of the experimental lattice parameters with those calculated on the basis of the crystal and alloy compositions. In the

calculations it was assumed that the lattice parameters vary linearly from AlB_2 to TiB_2. It is obvious that in the boride, as aluminum replaces titanium, the lattice parameter varies as assumed. This further confirms the expected continuous series of solid solutions from TiB_2 to AlB_2, for which the designation $(Al, Ti)B_2$ is appropriate. This is probably the phase that has been reported as the ternary compound. The existence of a mixed crystal explains the failure to obtain separation by the sink and float method. AlB_2 with a density of 3.16 g per cu cm should float on a 3.3 g per cu cm liquid, whereas $TiAl_3$ with 3.36 g per cu cm density should sink. An $(Al, Ti)B_2$ phase with a density closer to the 4.38 g per cu cm of TiB_2 than to 3.16 g per cu cm instead would sink together with the $TiAl_3$, as found. There is very limited correlation between the crystal and alloy composition, and it appears that the replacement of titanium by aluminum in the compound is not as rapid as would be expected from the composition of the melts. This could be interpreted as some special electronic effect, but actually must be attributed to nonequilibrium conditions. TiB_2 has a very high freezing point (2850°C). AlB_2 instead forms by peritectic reaction at a lower temperature (975°C). Thus, most probably, solidification starts with the formation of a titanium-rich boride and diffusion of aluminum into the solid crystal is necessary to bring the crystal to equilibrium composition.

In many samples with high alloy content in which equilibrium was not reached, a sheathing of the boride crystals was seen, as shown in Fig. 1. From the shape of the crystals, their etching characteristics and the X-ray patterns of the extracted crystals, this was identified as diffusion of the aluminum into the TiB_2 crystals. As the aluminum diffuses in, titanium diffuses out and combines with the surrounding aluminum to form a sheath of $TiAl_3$ around the $(Al, Ti)B_2$ crystal. Since this reaction is extremely slow, chances of obtaining equilibrium are very limited, unless the alloy is greatly diluted. This is also indicated by the fact that samples extracted from alloys of the same composition, but prepared at different times, show substantial differences

Table I. Composition and Lattice Parameters of Extracted Crystals

| Sample No. | Alloy Composition | | Crystal Composition | | | | | | Experimental | | Lattice Parameters Calc. on Composition of | | | |
| | | | Ti | | B | | Al | | | | Crystal | | Alloy | |
	Ti	B	Wt pct	at. pct	Wt pct	at. pct	Wt pct	at. pct	a	c	a	c	a	c
1	7.00	—	37.2*	25	—	—	62.8*	75	3.850	8.596	—	—	—	—
2	1.20	0.05	36.5	24.1	0.70	2.1	62.8	73.8	—	—	—	—	—	—
3	0.10	0.05	36.7	24.3	0.95	2.7	62.3	73.0	3.844	8.587	—	—	—	—
4	TiB_2	—	68.9*	33.3	31.1*	66.7	—	—	3.028	3.228	—	—	—	—
5	5.50	1.00	65.7	31.0	32.2	67.3	2.2†	1.7	3.028	3.228	3.0276	3.2284	3.0274	3.2291
6	5.50	1.00	—	—	—	—	—	—	3.029	3.228	—	—	3.0274	3.2291
7	2.75	1.60	66.9	31.7	32.1	67.5	1.0†	0.8	3.027	3.229	3.0278	3.2282	3.0241	3.2382
8	2.55	2.05	59.7	27.2	33.3	67.1	7.0	5.7	3.026	3.233	3.0259	3.2318	3.0233	3.2407
9	2.55	2.05	67.5	32.2	32.0	67.2	0.75†	0.6	3.028	3.228	3.0279	3.2282	3.0233	3.2407
10	2.20	1.92	—	—	—	—	—	—	3.029	3.229	—	—	3.0221	3.2422
11	1.73	2.50	53.7	23.8	34.2	66.9	12.1	9.4	3.025	3.235	3.0244	3.2344	3.0190	3.2462
12	1.10	2.56	—	—	—	—	—	—	3.028	3.225	—	—	3.0177	3.2482
13	1.10	2.56	—	—	—	—	—	—	3.027	3.230	—	—	3.0177	3.2482
14	0.50	2.98	14.5	5.3	41.2	65.9	44.3	28.8	3.015	3.250	3.0144	3.2558	3.0122	3.2543
15	—	3.10	—	—	44.5*	66.7	55.5*	33.3	3.010	3.262	—	—	—	—

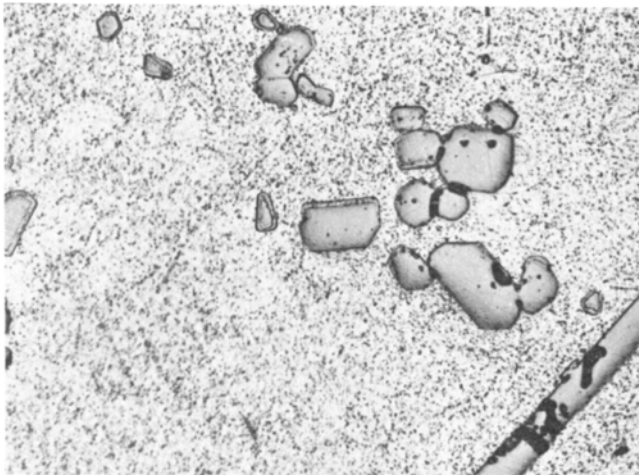*Nominal.
†Composition corrected for AlB_{12}.

Fig. 1—Alloy with 2 pct Ti, 2.5 pct B. Magnification 250 times. Keller's etch. Notice rim around most of the hexagonal crystals, but not around long needle of TiAl₃.
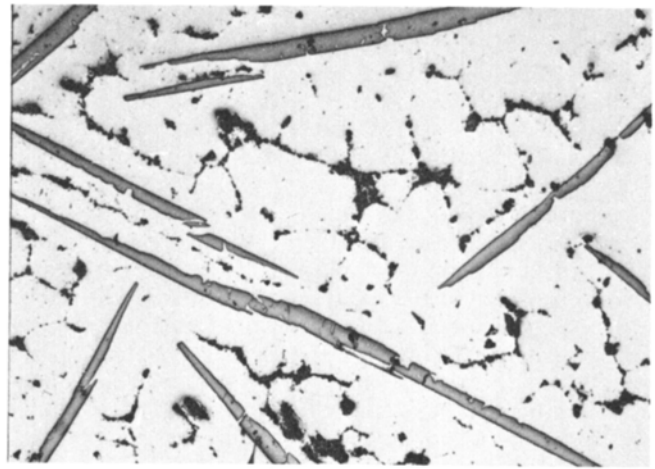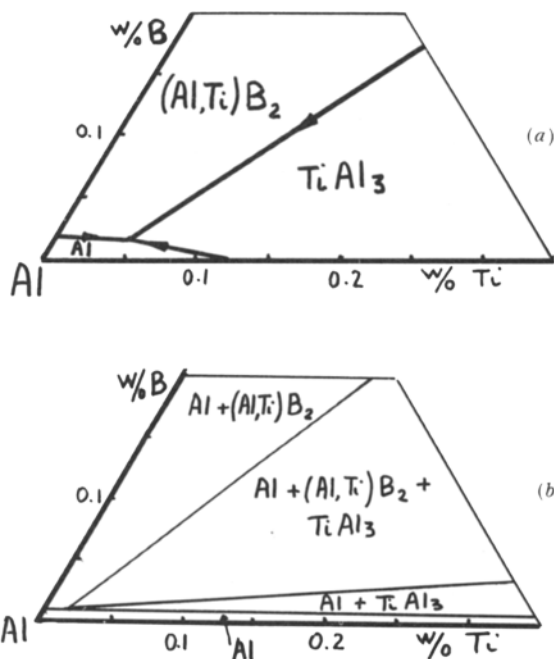

Fig. 2—Aluminum corner of the equilibrium diagram Al-B-Ti: (a) liquidus, (b) approximate boundaries of the various fields in the solid state at eutectic temperature.

Fig. 3—Alloy with 5 pct Ti, 1 pct B. Magnification 250 times, not etched.
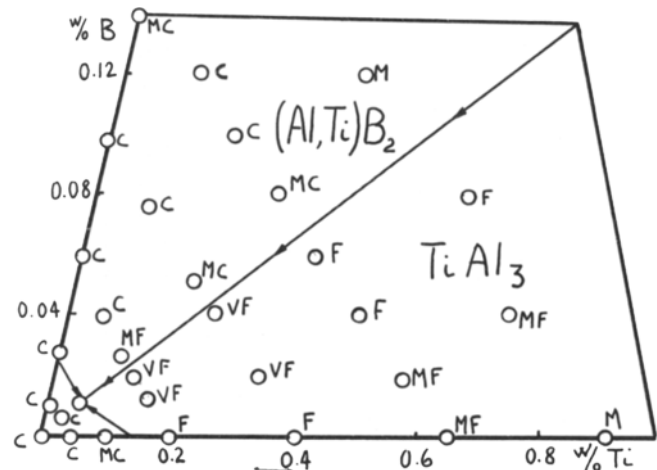

Fig. 4—Grain size of alloys as function of composition: C = Coarse, MC = Medium Coarse, M = Medium, MF = Medium Fine, F = Fine and VF = Very Fine. For examples see Fig. 5 — notice enlarged scale for pct B.

in aluminum content. Thus, it is probably more accurate to assume that, in equilibrium conditions, lattice parameters and composition of (Al, Ti)B₂ change regularly and continuously from TiB₂ to AlB₂.

On the basis of these data and the results of the determination of primary crystallization and freezing points, the diagrams in Fig. 2 have been drawn as the ones consistent with all the experimental results. The liquidus diagram shows 3 monovariant lines: Liq → Al + (Al, Ti)B₂, Liq → (Al, Ti)B₂ + TiAl₃, and a third line which starts as Liq + TiAl₃ → Al and changes to Liq → TiAl₃ + Al. These three lines meet at a eutectic point: Liq → Al + (Al, Ti)B₂ + TiAl₃. The eutectic temperature was found to be between 659° and 659.5°C and the maximum length of eutectic arrest was found when the composition of the liquid was approximately 0.05 ± 0.01 pct Ti, 0.01 ± 0.002 pct B. In this eutectic the

TiAl₃ phase may contain up to 1 pct B, the (Al, Ti)B₂ phase little or no aluminum, the aluminum phase less than 0.01 pct B and 0.05 pct Ti.

The results of the attempts to determine the liquidus of the ternary alloys at various temperatures by settling the primary crystals were too scattered for plotting of isotherms in the ternary fields but showed very definitely that even small amounts (<0.005 pct) of boron radically reduce the liquid solubility of titanium, especially at the high temperatures. Thus, the liquidus surfaces can be expected to rise sharply from the eutectic point.

The microstructure of the ternary eutectic is very coarse and typical of a divorced type. This is to be expected, since both TiAl₃ and (Al, Ti)B₂ can nucleate aluminum, but not each other. Thus, the ternary eutectic tends to split into two alloys: One containing TiAl₃ and aluminum which usually freezes first, and results in TiAl₃ crystals with a halo of aluminum, and the Al - (Al, Ti)B₂ eutectic which freezes last and forms the grain boundaries, Fig. 3.

It can be expected that in the solid state the solubility of titanium in aluminum is drastically curtailed even by very small amounts of boron. When TiAl₃ is
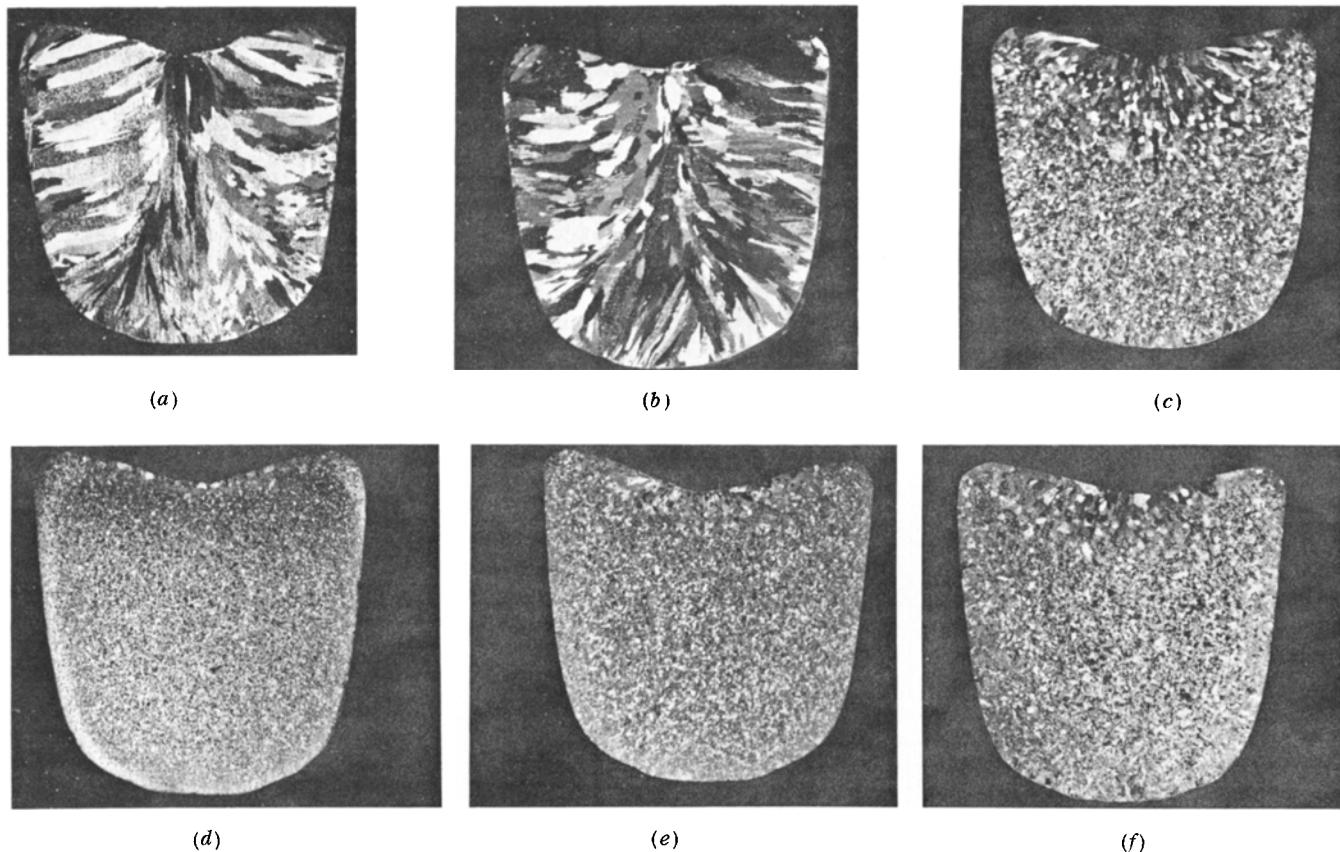
(a) (b) (c)

(d) (e) (f)

Fig. 5—Effect of Ti-B ratio on grain size. All samples natural size. (a) Coarse (C), 0.00 pct Ti, 0.06 pct B; (b) Coarse (C), 0.04 pct Ti, 0.04 pct B; (c) Medium fine (MF), 0.10 pct Ti, 0.025 pct B; (d) Very fine (VF), 0.12 pct Ti, 0.022 pct B; (e) Very fine (VF), 0.15 pct Ti, 0.001 pct B; (f) Fine (F), 0.20 pct Ti, 0.00 pct B.

present, the aluminum solid solution is in equilibrium with $(Al, Ti)B_2$ of undetermined composition and there is a very large two-phase field in which the Al_{ss} is in equilibrium with the solid solution series from TiB_2 to AlB_2. The solid solubilities of titanium and boron in aluminum can be expected to decrease with decreasing temperature, but it is doubtful that they will ever be determined accurately since years of annealing would be necessary to bring some semblance of equilibrium to the alloys.

2) Grain Refinement

The results of the effect of boron on grain refinement in aluminum-titanium alloys are shown in Fig. 4. In Fig. 5 is shown a series of alloys across the ternary diagram, which can be considered typical of the results obtained. Fig. 6 shows the grain size of an alloy in which crystals of TiB_2 were added. It should be noted that the alloys for these determinations were cycled several times from 900°C to the freezing point and back before being heated to 740°C and cast and, therefore, are closer to equilibrium than most other determinations in the literature.

As can be seen in the alloys with a low titanium/boron ratio little or no grain refinement takes place. Only when the titanium is at least four times the boron and the boundary between the primary fields of $TiAl_3$ and $(Al, Ti)B_2$ is reached, is there appreciable grain refinement. The grain refinement is maximum at the $Ti/B = 5$ ratio and decreases slightly as the ratio in-
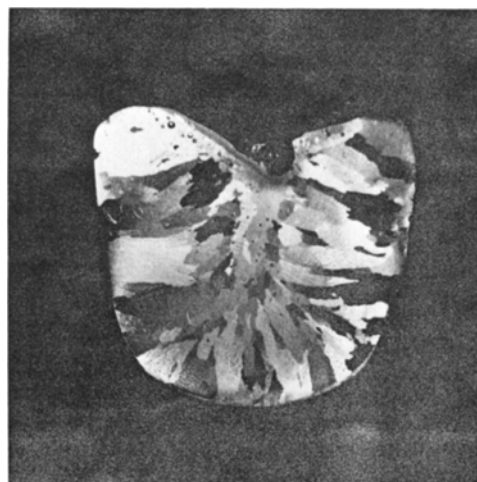

Fig. 6—Alloy with addition of TiB_2 crystals—natural size.

creases. Similar results were obtained at concentrations somewhat higher or lower, as indicated in Fig. 4. No substantial grain refinement was found at very low concentrations (in the field of primary crystallization of aluminum) and as the alloy content increased about 0.4 to 0.5 pct, the grain refinement tends to decrease. It is obvious that grain refinement is obtained only when $TiAl_3$ is primary, although both $TiAl_3$ and the borides can nucleate aluminum.

The basic difference between the nucleation by the two types of crystals is that, whereas $TiAl_3$ can nucleate
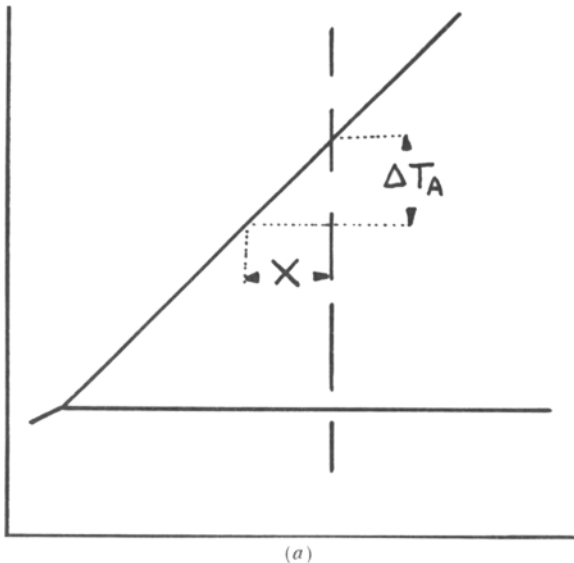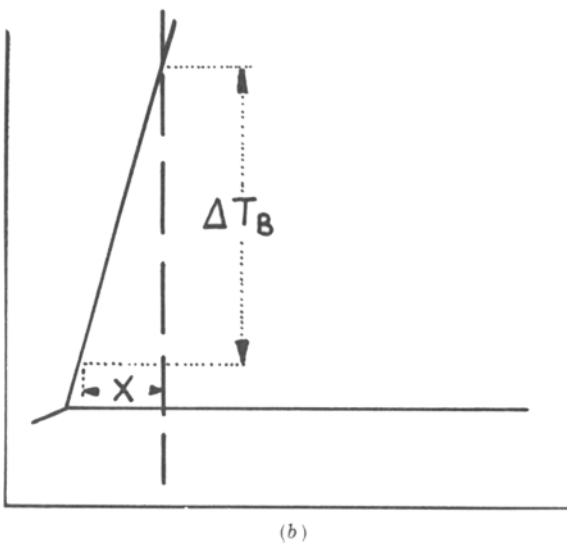
Fig. 7—Effect of liquidus slope on undercooling for nuclea-
tion—in (a) supersaturation X is reached with ΔT_A, in (b) the
same supersaturation is reached with the much larger ΔT_B.
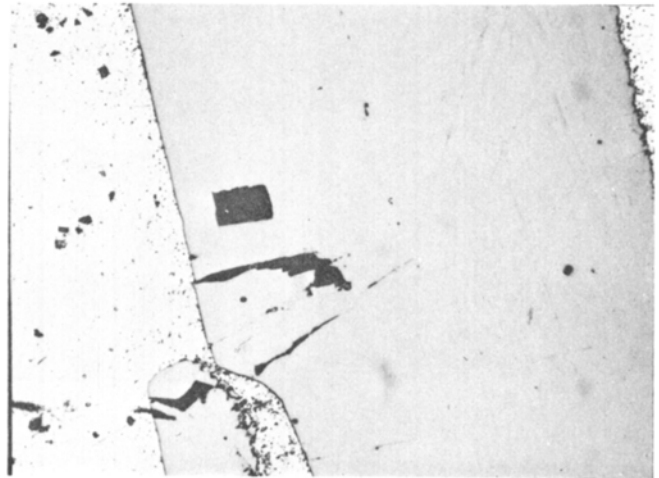

Fig. 8—Al-Ti alloy with TiC additions—magnification 250
times, not etched. Small dark crystal of TiC inside large
light crystal of TiAl$_3$, with probable orientation relationship
(100) ‖ (100); [001] ‖ [001].

aluminum solid solution without undercooling and in
most cases (through the peritectic reaction), at tem-
peratures above the freezing point of aluminum, AlB$_2$,
TiB$_2$ and (Al, Ti)B$_2$ require some undercooling below
the freezing point of aluminum to nucleate it.[12] Normal
impurities tend to nucleate aluminum with very limited
undercooling, thus the borides have little or no chance
to be effective nucleants.

The peritectic reaction facilitates grain refinement
by insuring nucleation of aluminum by TiAl$_3$ before the
normal impurities can act, but it is not necessary.
TiAl$_3$ can nucleate aluminum even when it is eutectic.
The only requirement for grain refinement, therefore,
is that TiAl$_3$ be present and active as a nucleant, be-
fore other impurities can nucleate.

The better grain refinement produced by addition of
boron to aluminum-titanium alloys is not due to nucle-
ation of aluminum by borides. Boron produces two ef-
fects:

1) It expands the field of primary crystallization of
TiAl$_3$ to lower titanium contents by reducing the solu-
bility of titanium in liquid aluminum. This results in
grain refinement at lower titanium contents.

2) Boron also steepens the slope of the liquidus. In
the liquid there are many solid particles which can
nucleate TiAl$_3$ at different undercoolings. If the liqui-
dus line is relatively flat, as shown in Fig. 7(a), a
slight undercooling (ΔT_A) produces a pronounced super-
saturation (X), which leads to nucleation on the availa-
ble heterogeneous centers. If the liquidus is very steep,
as in Fig. 7(b), the same supersaturation requires a
much larger undercooling (ΔT_B) that permits nucleation
not only on the same centers, but also on many other
centers that act at higher undercooling. In addition, the
time to cool from the temperature at which TiAl$_3$ is
nucleated to that at which it nucleates aluminum is
longer in case (a) and much more coagulation and
growth of TiAl$_3$ particles takes place, further reducing
the number of nuclei. This explains the more pro-
nounced grain refinement, as shown in Fig. 5, that is
obtained by boron additions.

The slow diffusion of titanium and boron into alumi-
num, even in the liquid state, accounts for the fact that
grain refinement is often found in alloys that are out-
side the field of primary crystallization of TiAl$_3$. In
nonequilibrium conditions, which prevail in commer-
cial practice and also in a large portion of the ex-
perimental work, the solution of the TiAl$_3$ crystals in-
to the melt could be incomplete, leaving sufficient cen-
ters for nucleation. The diffusion of aluminum into the
first boride crystals formed to transform them from
TiB$_2$ to (Al, Ti)B$_2$ with a TiAl$_3$ sheath also contributes
to the enhanced refinement, because of nucleation by
the TiAl$_3$ sheath. Good evidence of this reaction has
been obtained by Bäckerud.[13]

The few results obtained with Al-C-Ti alloys resem-
ble the results with Al-B-Ti. Small additions of carbon
enhance the grain refinment, large ones reduce or
eliminate it. No metallographic evidence of nucleation
of aluminum by the carbides was seen. The carbides
were unevenly and randomly distributed, sometimes
within the crystal, sometimes at the boundaries. A
structure that was found in several alloys is shown in
Fig. 8: A TiC crystal inside a TiAl$_3$ crystal, whose

shapes indicate a (100) ∥ (100); [001] ∥ [001] orientation relationship, suggestive of nucleation of TiAl$_3$ by TiC.

CONCLUSIONS

1) At the aluminum corner of the Al–B–Ti equilibrium diagram there is a ternary eutectic: Al – (Al, Ti)B$_2$ – TiAl$_3$ at approximately 0.05 pct Ti, 0.01 pct B, 659.5 ± 0.2°C.

2) AlB$_2$ and TiB$_2$ form a continuous series of solid solutions ranging from one compound to the other.

3) Additions of boron expand the field of primary crystallization of TiAl$_3$ toward lower titanium contents and steepen the liquidus.

4) Grain refinement is due to nucleation of the aluminum by TiAl$_3$ crystals and in equilibrium conditions is obtained only in alloys in which TiAl$_3$ is primary. Grain refinement in alloys outside the TiAl$_3$ primary field is due to nonequilibrium conditions.

5) The peritectic reaction facilitates nucleation by TiAl$_3$ before other impurities can nucleate, but it is not necessary for grain refinement.

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