Phase Equilibria Investigations on the Aluminum-Rich Part of the Binary System Ti-Al

J. BRAUN and M. ELLNER

The binary system Ti-Al has been reinvestigated in the composition range of 50 to 76 at. pct Al by X-ray diffraction, metallography, electron probe microanalysis (EPMA), and differential thermal analysis (DTA). Heat-treated alloys (600 °C to 1300 °C) as well as the as-cast alloys were investigated. Seven stable intermetallic phases were observed: TiAl, $Ti_{1-x}Al_{1+x}$, Ti_3Al_5, $TiAl_2$, Ti_5Al_{11}, $TiAl_3$ (h), and $TiAl_3$ (l); two metastable phases, $TiAl_2$ (m) and $TiAl_3$ (m), were also found. For each of these phases, the homogeneity range and the crystal chemical parameters were determined. The temperatures of the solid-state phase reactions were re-established. On the basis of the experimental results, an improved version of the equilibrium phase diagram has been drawn and critically compared with earlier versions presented in the literature.

I. INTRODUCTION

THE binary phase diagram Ti-Al is the basis for many alloys of technical importance, namely, for those based on the intermetallic compounds Ti_3Al[1] and γ-TiAl.[2,3] While the titanium-rich part of the system has been investigated extensively,[4–13] the aluminum-rich part is still not clear. Ogden *et al.*[14] and Bumps *et al.*[15] reported the initial versions of the Ti-Al phase diagram. These contain only two intermetallic compounds in the aluminum-rich part, TiAl and $TiAl_3$. Pötzschke and Schubert[16] found the phase $TiAl_2$ ($HfGa_2$ type). Raman and Schubert[17] inserted the high-temperature phase Ti_5Al_{11} and the low-temperature phase Ti_9Al_{23} in the phase diagram.

Afterward, Loiseau and Vannuffel[18] included the phase Ti_3Al_5 and found two structural modifications for the phase $TiAl_2$: $TiAl_2$ (I) ($ZrGa_2$ type) and $TiAl_2$ (II) ($HfGa_2$ type). In the composition range $TiAl_2$-$TiAl_3$, a great number of long period structures were also observed by Loiseau *et al.*,[19] especially in the high-temperature but also in the low-temperature region. Kaltenbach *et al.*[20] found only two intermediate phases between TiAl and $TiAl_3$: $TiAl_2$ and Ti_5Al_{11}. These authors also corrected the temperatures of the phase reactions.

The most recent phase diagram version for the aluminum-rich part of the Ti-Al system, which is based on extensive experimental work, has been elaborated by Schuster and Ipser.[21] These authors found seven intermetallic compounds in the composition range of 50 to 75 at. pct Al. They added the phase $Ti_{1-x}Al_{1+x}$, observed at 64 at. pct Al, into the high-temperature part of the phase diagram. The intermetallic compounds Ti_5Al_{11} and Ti_2Al_5 were incorporated as two separate phases in the high-temperature region of this system. However, no phase equilibria investigations have been made in the low-temperature region below 970 °C.

Calculated phase diagram versions of the Ti-Al system have been reported by Murray,[22] Kattner *et al.*,[23] and Zhang *et al.*[24] However, Murray[22] considered only the intermetallic phases TiAl and $TiAl_3$ in the aluminum-rich part of this system. Kattner *et al.*[23] made a calculation that included the phases Ti_2Al_5 and $TiAl_2$ with a low- and a high-temperature modification. Zhang *et al.*[24] yielded a calculation of the Ti-Al system based on an improved thermodynamic description of the intermetallic phases.

II. EXPERIMENT

The binary Ti-Al alloys (with a mass of approximately 3 g) were made from metals with the following purity: titanium 99.99 pct (Johnson Matthey Co.) and aluminum 99.999 pct (Vereinigte Aluminium-Werke). The alloys were produced by melting metals in an arc furnace in an argon atmosphere (Messer-Griesheim 5N). Chemical analysis of the melted alloys was not carried out because the weight loss was smaller than 0.5 wt. pct. For the heat-treatment procedures, the alloys were wrapped in thin tantalum foils and put in silica tubes, which were then evacuated and backfilled with 0.5 atm of argon. Most of the alloys were homogenized by a first heat treatment at 1200 °C for 5 to 12 hours or at 1250 °C for 4 hours.

The phase analysis was carried out by X-ray diffraction and microscopical investigations. For the X-ray powder diffraction, the bulk alloys were crushed and powdered in a mortar and heat treated in evacuated small silica tubes. The heat treatment of powders at higher temperatures (≥900 °C) was carried out in small tantalum tubes enclosed in evacuated silica tubes. A Guinier camera (Einraf Nonius FR 552) with Cu K_{α_1} radiation or Cr K_{α_1} radiation (for higher resolution) and single-coated CEA REFiLEX 15 film was used for the X-ray exposures. Diffraction angles and integrated intensities of diffraction lines were densitometrically obtained by means of the line scanner LS20 (KEiJ Instruments). Unit cell parameters were refined by the least-squares fitting of Bragg's equation.

The microstructural investigations of etched Ti-Al alloys were made by means of optical microscopy. The following etching solutions were applied: Keller mordant, a solution according to Kaltenbach *et al.*,[20] and a solution according to Costa Neto *et al.*[25] To distinguish very similar phases,

---

J. BRAUN, Postdoctoral Fellow, and M. ELLNER, Senior Research Associate, are with the Max-Planck-Institut für Metallforschung, D-70174 Stuttgart, Germany.

Manuscript submitted July 13, 2000.

a scanning electron microscope (SEM), (JEOL* JXA 6400) was used to observe backscattered electron images and to carry out the electron probe microanalysis (EPMA) of these phases.

The temperatures of the phase transformations were determined by differential thermal analysis (DTA) of heat-treated samples. In cases where the thermal effect was too small, the transformation temperature was narrowed by X-ray and by metallographical investigations of the heat treated samples.

III. RESULTS

A. *Overview of the Intermetallic Phases in the Aluminum-Rich Part of the System Ti-Al*

The intermetallic phases observed in this work are listed in Table I. For each phase, the homogeneity range and the temperature range of existence have been determined. Moreover, each phase has been prepared as single phase or nearly single phase. From these samples, the unit cell parameters have been measured. These are listed together with the crystal chemical parameters, such as the type of structure, Pearson symbol, and space group.

B. *As-Cast Alloys*

The results of the phase analysis of the liquid quenched alloys were reported previously.[26] Vertically oriented, large, and elongated primary crystals typically appear in the as-cast buttons. Most as-cast alloys contain several phases, some of which are not equilibrium phases for this composition.

The alloys with 50 and 52.5 at. pct Al contain TiAl together with the solid solution α-Ti(Al). Metallographic investigations show that dendrites with hexagonal symmetry crystallize from the melt with TiAl as residual phase in between. These dendrites transform into a fine-lamellar microstructure of Ti_3Al and TiAl.

The alloys in the composition range $Ti_{45}Al_{55}$ to $Ti_{38}Al_{62}$ show TiAl as single phase. The high-temperature phase $Ti_{1-x}Al_{1+x}$ has been found in the alloys of the composition range $Ti_{37}Al_{63}$ to $Ti_{35}Al_{65}$.

The orthorhombic phase $TiAl_2$ (m) ($ZrGa_2$ type) appears at the alloy compositions $Ti_{36}Al_{64}$ to $Ti_{32.7}Al_{67.3}$ together with $Ti_{1-x}Al_{1+x}$ or Ti_5Al_{11}. The phase $TiAl_2$ (m) occurs only in the as-cast state. Annealing treatments at temperatures up to 1200 °C lead to the transformation into the tetragonal phase $TiAl_2$ ($HfGa_2$ type). As a result of the heat treatments at temperatures above 1240 °C, $TiAl_2$ (m) transforms into the tetragonal phase Ti_5Al_{11}. With regard to these facts, $TiAl_2$ (m) has been considered to be a metastable phase (m = metastable).

The as-cast samples containing 70 to 74.75 at. pct Al show three phases: Ti_5Al_{11}, $TiAl_3$ (h), and the solid solution Al(Ti). The alloys in the composition range $Ti_{25}Al_{75}$ to $Ti_{20}Al_{80}$ contain two phases: the high-temperature phase $TiAl_3$ (h) and Al(Ti). The metastable phase $TiAl_3$ (m) (Cu_3Au type) was produced by means of liquid quenching.[26]

C. *Investigations of the Phase Equilibria in the Composition Range $Ti_{50}Al_{50}$ to $Ti_{35}Al_{65}$*

The phase equilibria in the aluminum-rich part of the Ti-Al system are shown in Figure 1 and Table II. The results of the X-ray and microstructural investigations concerning the composition range $Ti_{50}Al_{50}$ to $Ti_{35}Al_{65}$ are listed in Table III.

1. *The homogeneity range of TiAl*

Several contradictory versions of the homogeneity range of the intermediate phase TiAl have been reported; the discrepancy concerns the aluminum-rich phase boundary, in particular. Therefore, this part of the binary system Ti-Al has been reinvestigated in this work. The aluminum-rich boundary was determined by EPMA measurements on the two-phase alloys containing TiAl + $TiAl_2$ (Table IV); the microstructure of the alloy $Ti_{39}Al_{61}$ heat treated at 800 °C for 20 days is shown in Figure 2. The unit cell parameters for these alloys were also measured and compared with those for the single-phase TiAl (Reference 28, Table II); with these data, the phase boundary has also been established. Table IV shows the results of both methods, which are in good agreement. The macroscopic densities of alloys in the composition range 50 to 60 at. pct Al were reported previously.[28]

2. *The high-temperature phase $Ti_{1-x}Al_{1+x}$*

This phase occurs as a single phase in alloys of the composition range 63 to 65 at. pct Al at 1300 °C. The crystal structure of $Ti_{1-x}Al_{1+x}$ is homeotypical with that of TiAl. However, both phases are distinguishable if the intensity ratios of the X-ray reflex pairs $(hhl)/(hlh)$ with $h + l = 2n$ are considered. These are inverse in $Ti_{1-x}Al_{1+x}$ compared with TiAl. This observation corresponds to a significantly different distortion of the CuAu-type structure.[29] Whereas TiAl shows a c/a ratio > 1, in $Ti_{1-x}Al_{1+x}$, the axial ratio is <1 (Figure 4). The observed unit cell parameters are $a = 4.030$ (1) Å, $c = 3.955$ (1) Å, and $c/a = 0.981$ for $Ti_{36}Al_{64}$ and $a = 4.029$ (1) Å, $c = 3.958$ (1) Å, and $c/a = 0.982$ for $Ti_{37}Al_{63}$.

The phase $Ti_{1-x}Al_{1+x}$ decomposes eutectoidally at a temperature $1160\ °C < T_e < 1180\ °C$ into the phases TiAl and $TiAl_2$. The results of the microstructural and X-ray diffraction phase equilibria investigations are listed in Table III and inserted in the partial phase diagram in Figure 3. Metallographic investigation of the alloy $Ti_{36}Al_{64}$ (bulk 8 hours at 1200 °C, 1 hour at 1240 °C, water quenched) showed $Ti_{1-x}Al_{1+x}$ as single phase (Reference 29, Figure 1). The eutectoidal decomposition of $Ti_{1-x}Al_{1+x}$ is shown in the microstructure of the alloy $Ti_{36}Al_{64}$ heat-treated for 15 hours at 1100 °C (Figure 5).

3. *The stability of the phase Ti_3Al_5*

The phase Ti_3Al_5 is a low-temperature phase formed peritectoidally from TiAl and $TiAl_2$ at $800\ °C < T_p < 820\ °C$. It is observed as single phase at the composition $Ti_{38}Al_{62}$ and at temperatures $T < 800$ °C by both the metallographical and the X-ray investigations. Ti_3Al_5 was formed only if as-cast alloys or specimens annealed at high temperature ($T >$ 1200 °C) were thereafter heat treated at $T < 800$ °C. Any annealing treatment at intermediate temperatures between 800 °C and 1200 °C resulted in a two-phase equilibrium consisting of TiAl and $TiAl_2$. When such a sample was heat treated afterward at $T < 800$ °C, this state was retained without formation of Ti_3Al_5. However, Ti_3Al_5 can easily be overheated in short-run heat treatments as well as in the

---

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

Table I. Intermetallic Phases in the Binary System Ti-Al in the Composition Range 50 to 75 At. Pct Al and Their Crystal Chemical Parameters as Determined in This Work

Phase	Structure Type Pearson Symbol	Space Group	Homogeneity Range	Existence	At. Pct Al	*a* (Å)	*c* (Å)	$(c/a)_S$	Heat Treatment	Reference
TiAl	CuAu *tP*4	*P*4/*mmm*	50 to 62 at 1200 °C	stable from RT to the melt	50	4.000(1)	4.075(1)	1.019	b:1200 °C/12 h p:1000 °C/8 min	Braun *et al.*[28] this work
					62	3.984(1)	4.060(1)	1.019	b:1200 °C/10 h p:1100 °C/4 min	
Ti_3Al_5	Ti_3Al_5 *tP*32	(*P*4/*mbm*)	62	RT Phase ≤810 °C	62	11.293(2) (3.993) $a = 2\sqrt{2}a_S$	4.038(1)	1.011	b: 700 °C/45 days p: 700 °C/11 days	this work
$Ti_{1-x}Al_{1+x}$	CuAu *tP*4	*P*4/*mmm*	63 to 65 at 1250 °C	HT phase ≥1170 °C	64	4.030(1)	3.955(1)	0.981	b: 1300 °C/25 min p: 1300 °C/3 min	Braun *et al.*[29]
$TiAl_2$	$HfGa_2$ *tI*24	$I4_1/amd$	66 to 67 at 1100 °C	RT phase ≤1215 °C	66.7	3.970(1)	24.309(1) (4.052)	1.020	b: 1000 °C/1 day p: 700 °C/11 days	Braun *et al.*[32]
$TiAl_2$ (m)	$ZrGa_2$ *oC*12	*Cmmm*	≈66 to 67	metastable in as-cast alloys	66.7	a: 3.942(1) b: 12.131(2) (4.044)	4.016(1)		as-cast alloy not single phase	this work
Ti_5Al_{11}	CuAu super-structure*	tetragonal	66 to 71 at 1300 °C	HT phase ≥995 °C	66	3.953(1)**	4.104(1)**	1.038	b: 1300 °C/25 min p: 1300 °C/1 min	this work
					71	3.918(1)**	4.154(1)**	1.060	b: 1300 °C/25 min p: 1300 °C/1 min	this work
$TiAl_3$ (h)	$TiAl_3$ *tI*8	*I*4/*mmm*	74.5 to 75 at 1200 °C	HT phase ≥950 °C Ti-rich ≥735 °C Al-rich	75	3.849(1)	8.609(1) (4.305)	1.118	b: 1000 °C/1 day p: 1000 °C/5 min	this work
$TiAl_3$ (l)	*tI*32	*I*4/*mmm*	75	RT phase ≤950 °C Ti-rich ≤735 °C Al-rich	76	3.877(1)	33.828(2) (4.229)	1.091	b: 640 °C/23 days p: 620 °C/6 days not single-phase	this work
$TiAl_3$ (m)	Cu_3Au *cP*4	$Pm\bar{3}m$	75	metastable by splat cooling	85	3.972(1)	—	—	splat cooling rotating wing not single phase	Braun *et al.*[26]

RT = room temperature, and HT = high temperature.
b: bulk, and p: powder.
Substructure unit cell parameter in parentheses; s = substructure.
*See Section IV.
**These data are valid for the substructure.

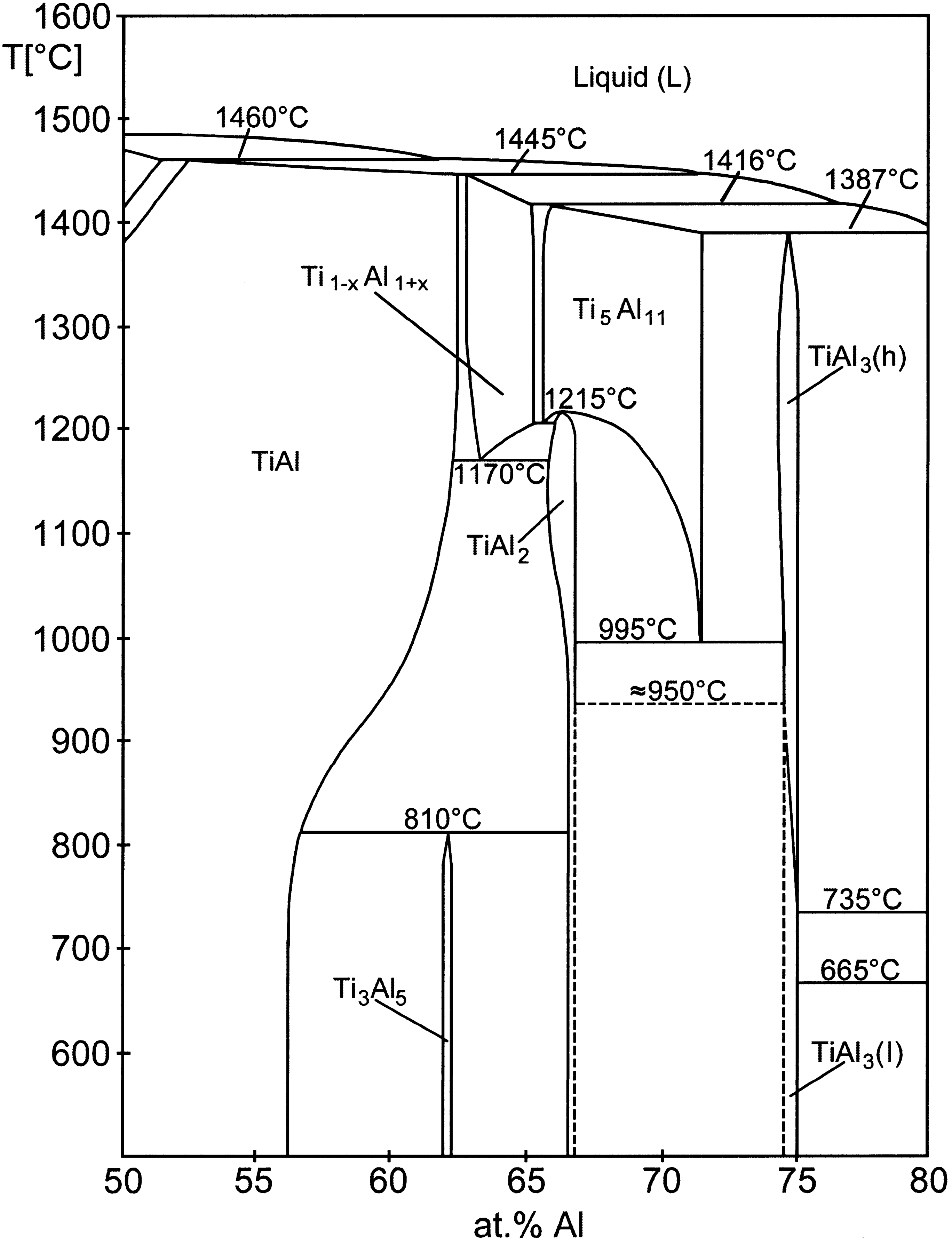

Fig. 1—Experimentally determined phase diagram Ti-Al in the composition range 50 to 80 at.% Al.

Table II. Invariant Phase Equilibria in the Aluminum-Rich Part of the Ti-Al System

Phase Reaction	Temperature, °C	Experimental Methods	Reference
Peritectic: $L + \alpha\text{-Ti(Al)} \rightleftharpoons \text{TiAl}$	1460	—	Schuster and Ipser [21]
Peritectic: $L + \text{TiAl} \rightleftharpoons \text{Ti}_{1-x}\text{Al}_{1+x}$	1445	—	Schuster and Ipser [21]
Peritectic: $L + \text{Ti}_{1-x}\text{Al}_{1+x} \rightleftharpoons \text{Ti}_5\text{Al}_{11}$	1416	—	Schuster and Ipser [21]
Peritectic: $L + \text{Ti}_5\text{Al}_{11} \rightleftharpoons \text{TiAl}_3$ (h)	1387	—	Schuster and Ipser [21]
Eutectoid: $\text{Ti}_{1-x}\text{Al}_{1+x} \rightleftharpoons \text{TiAl} + \text{TiAl}_2$	1170	X-ray and microstructure	this work
Peritectoid: $\text{TiAl} + \text{TiAl}_2 \rightleftharpoons \text{Ti}_3\text{Al}_5$	810	X-ray	this work
Polymorphic phase transformation: $\text{TiAl}_2 \rightleftharpoons \text{Ti}_5\text{Al}_{11}$	1215	X-ray and microstructure	this work, temperature: Schuster and Ipser[21]
Eutectoid: $\text{Ti}_5\text{Al}_{11} \rightleftharpoons \text{Ti}_{1-x}\text{Al}_{1+x} + \text{TiAl}_2$	≈1200	(X-ray) proposal	this work
Eutectoid: $\text{Ti}_5\text{Al}_{11} \rightleftharpoons \text{TiAl}_2 + \text{TiAl}_3$ (h)	995	X-ray and microstructure	this work
Peritectoid: $\text{TiAl}_2 + \text{TiAl}_3$ (h) $\rightleftharpoons \text{TiAl}_3$ (l)	≈950	X-ray	this work
Metatectic: TiAl_3 (h) $\rightleftharpoons \text{TiAl}_3$ (l) + L	735	DTA heat and X-ray	this work
Peritectic: $L + \text{TiAl}_3$ (h) $\rightleftharpoons$ Al(Ti)	665	—	Cissé *et al.*[27]

DTA measurements. At temperatures between 800 °C and 900 °C, rather long annealing times were necessary (*e.g.*, 830 °C: 16 hours; and 820 °C: 6 days) to decompose Ti_3Al_5 into TiAl and TiAl_2 completely. The DTA measurement for the determination of the peritectoid temperature on heating (5 K/min) yielded an effect at 876 °C. Additional heat treatments demonstrated that Ti_3Al_5 does not even exist below this temperature. Consequently, some more experiments have been carried out to determine the peritectoid temperature more exactly. These contain heat treatment and X-ray phase analysis of the alloy $\text{Ti}_{38}\text{Al}_{62}$. The initial state of the bulk sample heat treated at 700 °C for 45 days was single-phase Ti_3Al_5. Powders made from this sample were annealed at different temperatures in the temperature range 700 °C $\leq T \leq$ 930 °C for several days. X-ray phase analysis of these powder samples showed whether the phase Ti_3Al_5 was still present. As a result of these investigations, the invariant temperature has been set between 800 °C and 820 °C.

D. *Investigations of the Phase Equilibria in the Composition Range* $\text{Ti}_{34}\text{Al}_{66}$ *to* $\text{Ti}_{24}\text{Al}_{76}$

1. *Homogeneity range of* $\text{Ti}_5\text{Al}_{11}$ *and the eutectoid reaction* $\text{Ti}_5\text{Al}_{11} \rightleftharpoons \text{TiAl}_2 + \text{TiAl}_3$ *(h)*

The results are summarized in Table V and drawn in Figures 1 and 3. The phase $\text{Ti}_5\text{Al}_{11}$ shows a wide homogeneity range at high temperatures ($T > 1215$ °C), which reaches from 66 to 71 at. pct Al and includes the stoichiometries $\text{Ti}_5\text{Al}_{11}$ and Ti_2Al_5. Within this homogeneity range, the unit cell parameters and the positions of the superstructure lines were found to vary continuously with composition and temperature. The axial ratio c/a of the substructure increases linearly with the aluminum content (Figure 4). These results are in good agreement with those of Miida (Reference 30, Figure 12). The homogeneity range of $\text{Ti}_5\text{Al}_{11}$ is strongly reduced by the appearance of the phase TiAl_2 below 1215 °C, as can be seen in the partial phase diagram (Figure 3). TiAl_2 is formed by polymorphic phase transformation from $\text{Ti}_5\text{Al}_{11}$ at 1215 °C (temperature taken from Reference 21 and confirmed in this work) and at the stoichiometric composition of 66.7 at. pct Al. A two-phase region of TiAl_2 and $\text{Ti}_5\text{Al}_{11}$ reaches down to the temperature of the eutectoidal decomposition $\text{Ti}_5\text{Al}_{11} \rightleftharpoons \text{TiAl}_2 + \text{TiAl}_3$ (h) at 995 °C and 71.5 at. pct Al because of the reduced solubility of $\text{Ti}_5\text{Al}_{11}$ with decreasing temperature. Figure 6 shows the two-phase microstructure of $\text{Ti}_5\text{Al}_{11}$ with oriented precipitates of TiAl_2 in the alloy $\text{Ti}_{32.7}\text{Al}_{67.3}$ annealed at 1100 °C for 15 hours.

The high-temperature phase $\text{Ti}_5\text{Al}_{11}$ decomposes eutectoidally into TiAl_2 and TiAl_3 (h). The determination of the eutectoidal temperature is difficult because this reaction shows a strong tendency to be undercooled. In most cases, a part of the $\text{Ti}_5\text{Al}_{11}$ remains untransformed. Figure 7 shows the microstructure of the alloy $\text{Ti}_{29}\text{Al}_{71}$ heat treated at 950 °C for 11 hours. It represents the following typical microstructure: one part of the $\text{Ti}_5\text{Al}_{11}$ phase decomposes eutectoidally into TiAl_2 and TiAl_3 (h), while in the other part, $\text{Ti}_5\text{Al}_{11}$ remains untransformed with fine, oriented precipitates of TiAl_2 within the grains. The extent of the undercooling of the phase $\text{Ti}_5\text{Al}_{11}$ up to the onset of the eutectoidal transformation and the amount of the phase that is transformed depend on the alloy composition. The amount of untransformed $\text{Ti}_5\text{Al}_{11}$ (with precipitates of TiAl_2) increases with the aluminum content of the alloy investigated. In the alloy $\text{Ti}_{31}\text{Al}_{69}$, a heat treatment at 990 °C for 5 days led to a partial transformation, whereas in the alloy $\text{Ti}_{28}\text{Al}_{72}$, there was none, even after heat treatment at 970 °C for 5 days. Annealing at 900 °C for 9 days resulted in the total transformation of the alloy of composition $\text{Ti}_{31}\text{Al}_{69}$. A consecutive heat treatment at 980 °C for 2 days transformed TiAl_3 (l) (Section D–2) into TiAl_3 (h) and led to the two-phase microstructure of TiAl_2 and TiAl_3 (h) shown in Figure 8.

The eutectoidal transformation temperature could not be determined with DTA measurements because no thermal effect was observed. This temperature was narrowed stepwise by annealing experiments using both decreasing and increasing temperatures. With decreasing temperatures, undercooling phenomena have to be taken into account. With increasing temperatures, the formation of the phase $\text{Ti}_5\text{Al}_{11}$ occurs for the first time at 1000 °C in the alloys $\text{Ti}_{28}\text{Al}_{72}$ and $\text{Ti}_{27}\text{Al}_{73}$. In the more titanium-rich alloys $\text{Ti}_{30}\text{Al}_{70}$ and $\text{Ti}_{31}\text{Al}_{69}$, the phase $\text{Ti}_5\text{Al}_{11}$ does not arise before 1035 °C, presumably because of difficulties with nucleus formation. Combination and extrapolation of all these results leads to the deduction that the eutectoidal temperature has to be fixed between 990 °C and 1000 °C.

2. *The polymorphic phase transformation* TiAl_3 *(h)* $\rightleftharpoons$ TiAl_3 *(l)*

The phase TiAl_3 (h) appears at 75 at. pct Al and shows a noticeable but narrow homogeneity range at high tempera-

Table III. Result of the X-ray and Microstructure Phase Analysis in the Composition Range $Ti_{50}Al_{50}$ to $Ti_{35}Al_{65}$

Alloy Composition	Heat-Treatment Bulk Alloys*	Phase(s)
$Ti_{50}Al_{50}$	1200 °C/2 days	TiAl
$Ti_{47.5}Al_{52.5}$	1200 °C/12 h	TiAl
$Ti_{45}Al_{55}$	1200 °C/10 h	TiAl
	1000 °C/1 day	TiAl
	750 °C/10 days	TiAl
$Ti_{42.5}Al_{57.5}$	1200 °C/10 h	TiAl
$Ti_{40}Al_{60}$	1200 °C/10 h	TiAl
	1000 °C/1 day	TiAl
	900 °C/5 days	TiAl, $TiAl_2$
	800 °C/20 days	TiAl, $TiAl_2$
$Ti_{39}Al_{61}$	1300 °C/30 min	TiAl
	1250 °C/4 h	TiAl
	1200 °C/10 h	TiAl
	1100 °C/15 h	TiAl
	1000 °C/36 h	TiAl, $TiAl_2$
	900 °C/5 days	TiAl, $TiAl_2$
	800 °C/20 days	TiAl, $TiAl_2$
$Ti_{38}Al_{62}$	1300 °C/30 min	TiAl
	1250 °C/4 h	TiAl
	1200 °C/10 h	TiAl
	1100 °C/15 h	TiAl, $TiAl_2$
	1000 °C/36 h	TiAl, $TiAl_2$
	850 °C/5 days	TiAl, $TiAl_2$
	770 °C/10 days	Ti_3Al_5
	700 °C/45 days	Ti_3Al_5
	600 °C/90 days	Ti_3Al_5
$Ti_{37}Al_{63}$	1300 °C/30 min	$Ti_{1-x}Al_{1+x}$
	1250 °C/4 h	$Ti_{1-x}Al_{1+x}$
	1200 °C/10 h	$Ti_{1-x}Al_{1+x}$
	1100 °C/15 h	TiAl, $TiAl_2$
	900 °C/5 days	TiAl, $TiAl_2$
$Ti_{36}Al_{64}$	1300 °C/25 min	$Ti_{1-x}Al_{1+x}$
	1250 °C/4 h	$Ti_{1-x}Al_{1+x}$
	1240 °C/1 h	$Ti_{1-x}Al_{1+x}$
	1200 °C/8 h	$Ti_{1-x}Al_{1+x}$
	1180 °C/9 h	$Ti_{1-x}Al_{1+x}$, $TiAl_2$
	1160 °C/12 h	TiAl, $TiAl_2$
	1100 °C/15 h	TiAl, $TiAl_2$
$Ti_{35}Al_{65}$	1300 °C/25 min	$Ti_{1-x}Al_{1+x}$
	1250 °C/4 h	$Ti_{1-x}Al_{1+x}$
	1240 °C/1 h	$Ti_{1-x}Al_{1+x}$
	1200 °C/8 h	$Ti_{1-x}Al_{1+x}$, $TiAl_2$
	1100 °C/15 h	TiAl, $TiAl_2$

*The powder was heat treated at the same temperature for a short time.

Table IV. Determination of the Aluminum-Rich Phase Boundary of TiAl at Various Temperatures by EPMA and by X-ray Unit Cell Parameter Measurements

Temperature (°C)	EPMA (At. Pct Al)	X-Ray (At. Pct Al)
1100	61.7	—
1000	59.8	60.0
900	57.9	57.5
800	56.3	56.0

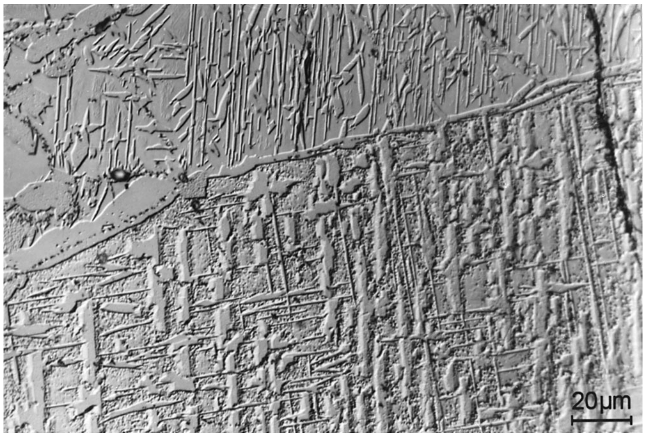

Fig. 2—Microstructure of the alloy $Ti_{39}Al_{61}$, bulk alloy 1200 °C/10 h + 1000 °C/36 h + 800 °C/20 days, etched with a mordant according to Kaltenbach, TiAl with precipitates of $TiAl_2$.

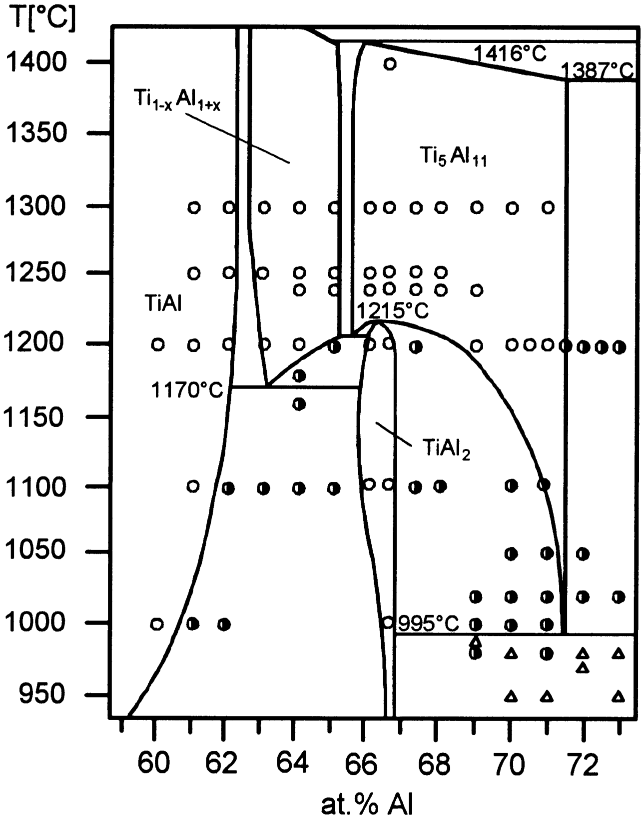

Fig. 3—Partial phase diagram Ti-Al in the composition range 59 to 73 at.% Al; ○ = single-phase sample, ◑ = two-phase sample, and △ = three-phase sample.

tures. This phase has been observed as single phase in the alloys $Ti_{25}Al_{75}$, $Ti_{25.25}Al_{74.75}$, and $Ti_{25.5}Al_{74.5}$ heat treated at 1200 °C for 5 hours by metallographical and powder diffraction investigations. The homogeneity range decreases at lower temperatures, which leads to the precipitation of Ti_5Al_{11} from $TiAl_3$ (h) (Figure 9).

At lower temperatures, $TiAl_3$ (h) transforms into $TiAl_3$ (l), but this reaction proceeds very sluggishly and incompletely. This reaction can be schematically subdivided in a sequence of a peritectoid and a metatectic reaction (Figure 10):

$$\text{peritectoid: } TiAl_2 + TiAl_3\,(h) \rightleftharpoons TiAl_3\,(l)$$

$$\text{metatectic: } TiAl_3\,(h) \rightleftharpoons TiAl_3\,(l) + \text{liquid}$$

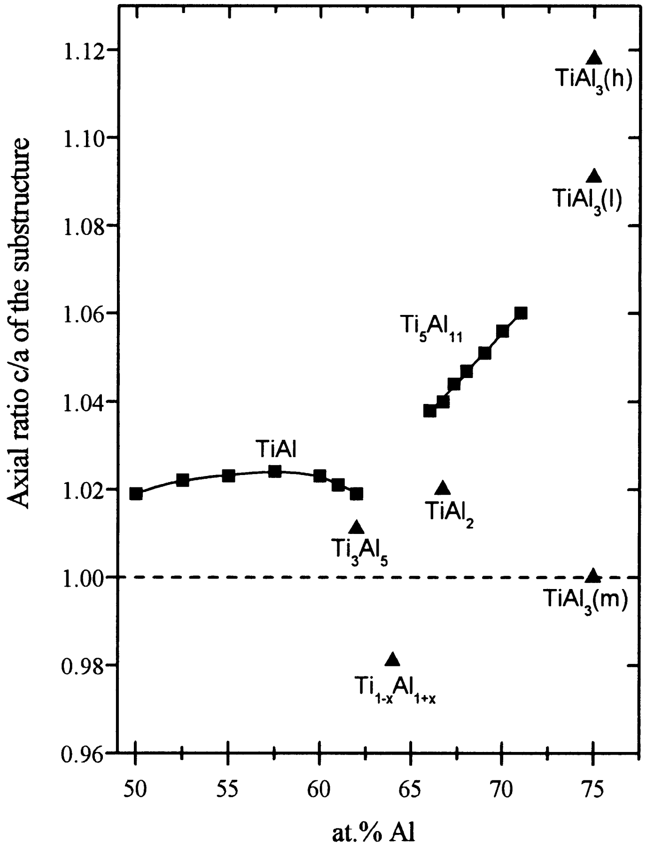

Fig. 4—Axial ratio *c/a* of the substructure for all crystal structures of the Ti-Al system belonging to the Cu family as a function of the aluminum content.

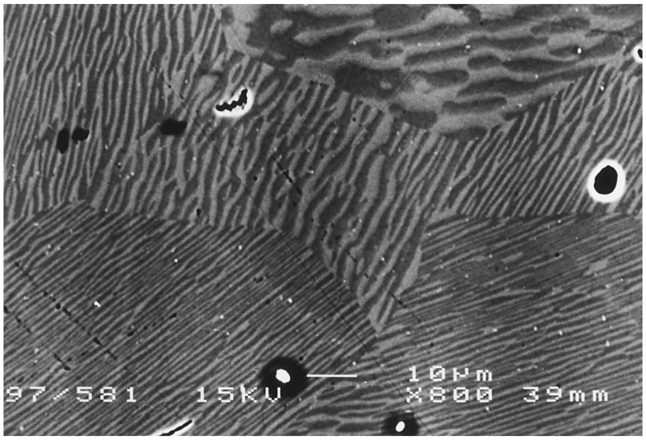

Fig. 5—Microstructure of the alloy $Ti_{36}Al_{64}$, bulk alloy 1250 °C/4 h + 1100 °C/15 h, SEM backscattered electron micrograph, eutectoid consisting of TiAl and $TiAl_2$.

Figure 11 presents a microstructure showing $TiAl_3$ (h) mainly transformed into $TiAl_3$ (l). The temperature of this polymorphic phase transformation is found to be much higher for the titanium-rich $TiAl_3$ (≈950 °C) than for the aluminum-rich $TiAl_3$ alloys (735 °C). The latter temperature of this phase transformation has been measured by the heating DTA investigations (5 K/min); it is in good agreement with the results of X-ray and microstructural investigations made on heat treated alloys. In contrast, no DTA effect was observed in the titanium-rich alloys near the stoichiometry $TiAl_3$. Moreover, the $TiAl_3$ modifications cannot be distinguished by optical or scanning electron microscopy except for nearly stoichiometric alloys. Therefore, the transformation temperature was estimated from the results of the X-ray investigations (Guinier patterns) done on heat treated alloys. In bulk alloys, $TiAl_3$ (l) was not observed after annealing at 950 °C, but was observed at 900 °C and at lower temperatures. However, in a series of powder-annealing experiments with the alloy $Ti_{26}Al_{74}$ bulk: 730 °C/51 days, the phase $TiAl_3$ (l) was still found at 960 °C, but disappeared at 1000 °C. With these results, the transformation temperature for titanium-rich $TiAl_3$ was set at nearly 950 °C.

In the composition range $TiAl_2$ to $TiAl_3$ in the low-temperature region, it is difficult to achieve equilibrium even after long-term heat treatments of up to 180 days. Moreover, the results of the X-ray and the microscopic investigations do not coincide. The Guinier patterns often show $TiAl_2$ together with the high- and low-temperature modification of $TiAl_3$, whereas the optical micrographs show $TiAl_2$, $TiAl_3$, and the remaining Ti_5Al_{11}. However, in a few experiments, the two-phase equilibrium of the phases $TiAl_2$ and $TiAl_3$ (l) was achieved: in the alloy $Ti_{30}Al_{70}$ bulk: 600 °C/20 days + 1200 °C/8 h + 1050 °C/13 h, powder: 700 °C/21 days, and in the alloy $Ti_{27}Al_{73}$ bulk: 600 °C/20 days + 1200 °C/6 h, powder: 700 °C/28 days.

The composition of the low-temperature modification of $TiAl_3$ does not differ from that of the high-temperature modification, as confirmed by EPMA measurements. Consequently, it is warrantable to denominate the low-temperature modification $TiAl_3$ (1) in contradiction to other designations given in the literature.

IV. DISCUSSION

The phase TiAl shows a relatively wide homogeneity range, as was already detected by Ogden *et al.*[14] These authors set the aluminum-rich boundary at about 60 at. pct Al, independent of the temperature. A similar phase boundary is drawn in the phase diagram of Schuster and Ipser.[21] In contrast to this, Bumps *et al.*[15] found a strong temperature dependency of the aluminum-rich boundary decreasing from more than 70 at. pct Al at 1350 °C to 59 at. pct Al at temperatures below 1000 °C. This tendency has been confirmed by the present investigations. However, at high temperatures ($T \geq 1200$ °C), the homogeneity range only reaches the composition of 62 at. pct Al because of the occurence of the phase $Ti_{1-x}Al_{1+x}$.

Schuster and Ipser[21] were the first to find the high-temperature phase $Ti_{1-x}Al_{1+x}$ in the as-cast samples. According to them, this phase is formed by a peritectic reaction from the melt and TiAl at 1445 °C, and decomposes at 1424 °C into TiAl and $TiAl_2$ (m). These authors did not carry out any heat treatment in the temperature range 1200 °C $< T <$ 1400 °C, and so could not observe $Ti_{1-x}Al_{1+x}$ in any annealed sample. Our investigations have shown that $Ti_{1-x}Al_{1+x}$ is still present in annealed specimens at 1180 °C. At 1160 °C, $Ti_{1-x}Al_{1+x}$ is decomposed eutectoidally into TiAl and $TiAl_2$. Therefore, the eutectoidal temperature has been set at 1170 °C.

The phase Ti_3Al_5 was observed by Miida *et al.*[31] after annealing an alloy $Ti_{37}Al_{63}$ at 700 °C for 11 days. Loiseau and Vannuffel[18] inserted this phase with an existence up to

Table V. Result of the X-ray and Microstructure Phase Analysis in the Composition Range $Ti_{34}Al_{66}$ to $Ti_{24}Al_{76}$

Alloy Composition	Heat-Treatment Bulk Alloys*	Phase(s)
$Ti_{34}Al_{66}$	1300 °C/30 min	Ti_5Al_{11}
	1250 °C/4 h	Ti_5Al_{11}
	1240 °C/1 h	Ti_5Al_{11}
	1200 °C/8 h	$TiAl_2$
	1100 °C/15 h	$TiAl_2$
$Ti_{33.3}Al_{66.7}$	1400 °C/15 min	Ti_5Al_{11}
	1300 °C/25 min	Ti_5Al_{11}
	1250 °C/4 h	Ti_5Al_{11}
	1240 °C/1 h	Ti_5Al_{11}
	1200 °C/8 h	$TiAl_2$
	1100 °C/15 h	$TiAl_2$
	1000 °C/1 day	$TiAl_2$
	750 °C/10 days	$TiAl_2$
$Ti_{32.7}Al_{67.3}$	1300 °C/25 min	Ti_5Al_{11}
	1250 °C/4 h	Ti_5Al_{11}
	1240 °C/1 h	Ti_5Al_{11}
	1200 °C/8 h	Ti_5Al_{11}, $TiAl_2$
	1100 °C/15 h	Ti_5Al_{11}, $TiAl_2$
$Ti_{32}Al_{68}$	1300 °C/25 min	Ti_5Al_{11}
	1250 °C/4 h	Ti_5Al_{11}
	1240 °C/1 h	Ti_5Al_{11}
	1100 °C/15 h	Ti_5Al_{11}, $TiAl_2$
	1000 °C/4 days	Ti_5Al_{11}, $TiAl_2$
$Ti_{31}Al_{69}$	1300 °C/25 min	Ti_5Al_{11}
	1240 °C/1 h	Ti_5Al_{11}
	1200 °C/8 h	Ti_5Al_{11}
	1020 °C/4 days	Ti_5Al_{11}, $TiAl_2$
	1000 °C/3 days	Ti_5Al_{11}, $TiAl_2$
	990 °C/5 days	$TiAl_2$, $TiAl_3$ (h), Ti_5Al_{11}
	980 °C/2 days	$TiAl_2$, $TiAl_3$ (h)
$Ti_{30}Al_{70}$	1300 °C/25 min	Ti_5Al_{11}
	1200 °C/8 h	Ti_5Al_{11}
	1100 °C/9 h	Ti_5Al_{11}, $TiAl_2$
	1050 °C/13 h	Ti_5Al_{11}, $TiAl_2$
	1020 °C/4 days	Ti_5Al_{11}, $TiAl_2$
	1000 °C/1 day	Ti_5Al_{11}, $TiAl_2$
$Ti_{29.5}Al_{70.5}$	1200 °C/8 h	Ti_5Al_{11}
$Ti_{29}Al_{71}$	1300 °C/25 min	Ti_5Al_{11}
	1200 °C/8 h	Ti_5Al_{11}
	1100 °C/9 h	Ti_5Al_{11}, $TiAl_2$
	1050 °C/13 h	Ti_5Al_{11}, $TiAl_2$
	1020 °C/4 days	Ti_5Al_{11}, $TiAl_2$
	1000 °C/1 day	Ti_5Al_{11}, $TiAl_2$
$Ti_{28.5}Al_{71.5}$	1200 °C/8 h	Ti_5Al_{11}, $TiAl_3$ (h)
$Ti_{28}Al_{72}$	1200 °C/7 h	Ti_5Al_{11}, $TiAl_3$ (h)
	1050 °C/2 days	Ti_5Al_{11}, $TiAl_3$ (h)
	1020 °C/4 days	Ti_5Al_{11}, $TiAl_3$ (h)
$Ti_{27.5}Al_{72.5}$	1200 °C/7 h	Ti_5Al_{11}, $TiAl_3$ (h)
$Ti_{27}Al_{73}$	1200 °C/7 h	Ti_5Al_{11}, $TiAl_3$ (h)
	1020 °C/4 days	Ti_5Al_{11}, $TiAl_3$ (h)
$Ti_{26.5}Al_{73.5}$	1200 °C/6 h	$TiAl_3$ (h), Ti_5Al_{11}
$Ti_{26}Al_{74}$	1200 °C/6 h	$TiAl_3$ (h), Ti_5Al_{11}
	1100 °C/14 h	$TiAl_3$ (h), Ti_5Al_{11}
	1020 °C/4 days	$TiAl_3$ (h), Ti_5Al_{11}
$Ti_{25.5}Al_{74.5}$	1200 °C/5 h	$TiAl_3$ (h)
	1100 °C/14 h	$TiAl_3$ (h), Ti_5Al_{11}
	640 °C/23 days	$TiAl_3$ (l), $TiAl_3$ (h), $TiAl_2$
	620 °C/105 days	$TiAl_3$ (l), $TiAl_3$ (h), $TiAl_2$
	600 °C/120 days	$TiAl_3$ (l), $TiAl_3$ (h), $TiAl_2$
$Ti_{25.25}Al_{74.75}$	1200 °C/5 h	$TiAl_3$ (h)
	620 °C/105 days	$TiAl_3$ (l), $TiAl_3$ (h)
	600 °C/120 days	$TiAl_3$ (l), $TiAl_3$ (h)
$Ti_{25}Al_{75}$	1200 °C/5 h	$TiAl_3$ (h)
	1100 °C/16 h	$TiAl_3$ (h)
	1000 °C/1 day	$TiAl_3$ (h)
	800 °C/17 days	$TiAl_3$ (h)
	770 °C/19 days	$TiAl_3$ (h)
	750 °C/37 days	$TiAl_3$ (h)
	720 °C/20 days	$TiAl_3$ (l), $TiAl_3$ (h)
	700 °C/17 days	$TiAl_3$ (l), $TiAl_3$ (h)
	640 °C/23 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
	620 °C/105 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
	600 °C/180 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
$Ti_{24.75}Al_{75.25}$	620 °C/105 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
	600 °C/180 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
$Ti_{24.5}Al_{75.5}$	640 °C/23 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
	620 °C/105 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
	600 °C/180 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
$Ti_{24}Al_{76}$	770 °C/3 days	$TiAl_3$ (h), Al (Ti)
	750 °C/3 days	$TiAl_3$ (h), Al (Ti)
	640 °C/23 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)
	600 °C/58 days	$TiAl_3$ (l), $TiAl_3$ (h), Al (Ti)

*The powder was heat treated at the same temperature for a short time.

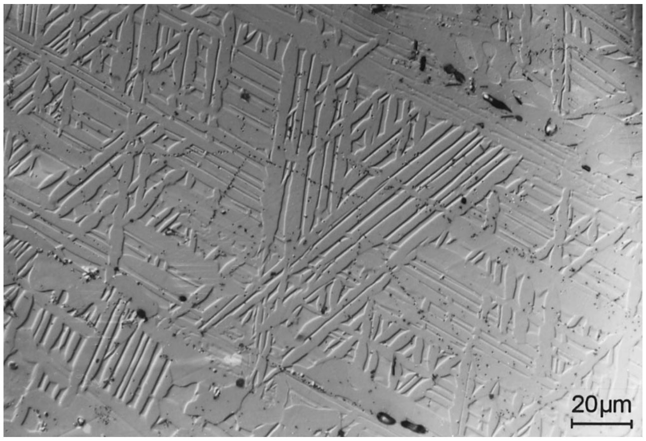

Fig. 6—Microstructure of the alloy $Ti_{32.7}Al_{67.3}$, bulk alloy 1250 °C/4 h + 1100 °C/15 h, etched with a mordant according to Kaltenbach, difference interference contrast, Ti_5Al_{11} with precipitates of $TiAl_2$.

1350 °C, where it should originate directly from TiAl. Neither Schuster and Ipser[21] nor Kaltenbach *et al.*[20] could find this phase because they did no heat treatment in the low-temperature range below 970 °C and 900 °C, respectively. In the present study, it was clarified that Ti_3Al_5 forms peritectoidally from TiAl and $TiAl_2$ at 810 °C. To obtain this phase, a purposeful annealing strategy is necessary. The phases $TiAl_2$ and $TiAl_2$ (m) are discussed extensively in another article.[32]

A phase called Ti_5Al_{11} was first described by Raman and Schubert[17] in the as-cast alloy $Ti_{31}Al_{69}$ as well as after annealing at 1160 °C for 2 hours. According to the phase diagram of these authors,[17] the phase Ti_5Al_{11} forms peritectically and decomposes eutectoidally into $TiAl_2$ and $TiAl_3$

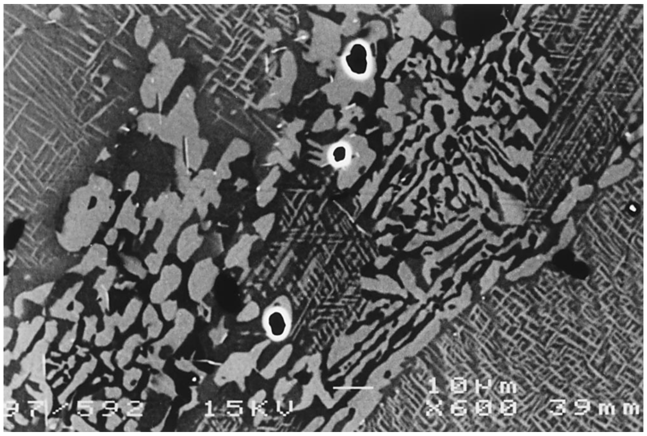

Fig. 7—Microstructure of the alloy $Ti_{29}Al_{71}$, bulk alloy 1200 °C/8 h + 950 °C/11 h, SEM backscattered electron micrograph, Ti_5Al_{11} (gray) with fine oriented precipitates of $TiAl_2$ (light gray) and eutectoid consisting of $TiAl_2$ and $TiAl_3$ (h) (dark).

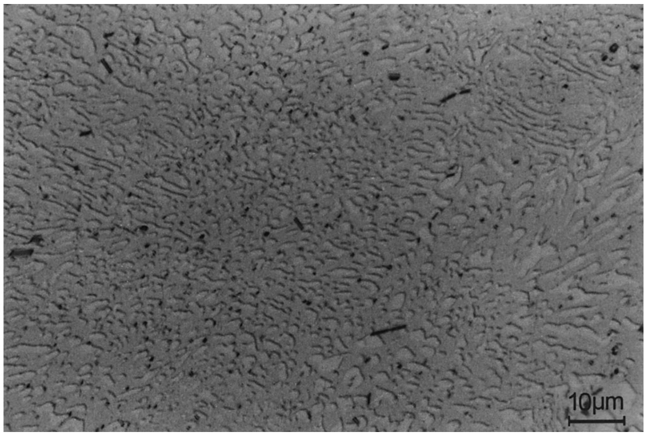

Fig. 8—Microstructure of the alloy $Ti_{31}Al_{69}$, bulk alloy 1200 °C/8 h + 900 °C/9 days + 980 °C/2 days, etched with Keller mordant, eutectoid consisting of $TiAl_2$ and $TiAl_3$ (h).

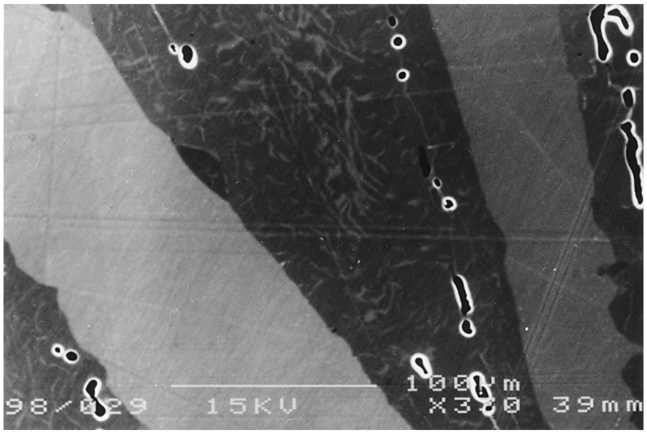

Fig. 9—Microstructure of the alloy $Ti_{27}Al_{73}$, bulk alloy 650 °C/6 days + 1200 °C/8 h + 1020 °C/4 days, SEM backscattered electron micrograph, Ti_5Al_{11} (light gray) and $TiAl_3$ (*h*) (dark) with precipitates of Ti_5Al_{11}.

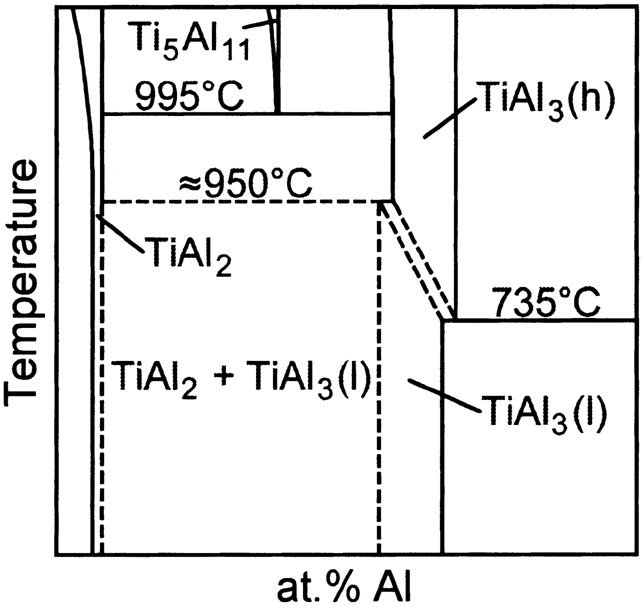

Fig. 10—Schematic partial phase diagram Ti-Al in the region around the polymorphic phases $TiAl_3$ (h) and $TiAl_3$ (l).

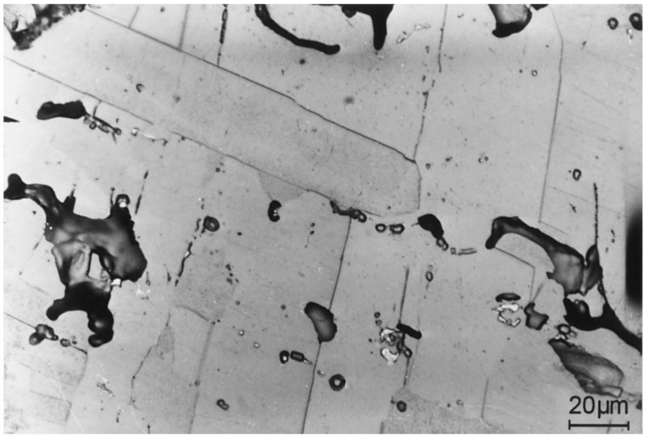

Fig. 11—Microstructure of the alloy $Ti_{25}Al_{75}$, bulk alloy 620 °C/105 days, etched with a mordant according to Kaltenbach, $TiAl_3$ (h) nearly completely transformed into $TiAl_3$ (l), and a little Al(Ti) (white).

at 950 °C. Van Loo and Rieck[33] investigated diffusion couples and found the phase Ti_2Al_5 after annealing at 1200 °C. Loiseau *et al.*[19] described a great number of high-temperature long period structures in the composition range of 71 to 73 at. pct Al, which were investigated and characterized by electron diffraction and high resolution electron microscopy. According to the phase diagram proposed by Loiseau *et al.*,[19] these long period structures are only stable above 1000 °C. Miida *et al.*[34] reported one-dimensional antiphase domain structures for alloys containing 67.5 to 73.5 at. pct Al heat treated at 1200 °C. Kaltenbach *et al.*[20] observed the phase Ti_5Al_{11} at 1100 °C but not at 900 °C. The eutectoid decomposition temperature could not be measured by DTA. For the phase diagram, Kaltenbach *et al.*[20] estimated the temperature given by Loiseau *et al.*[19] (990 °C) to be the most reliable. Schuster and Ipser[21] found two separate phases in the composition range of 68 to 72 at. pct Al at high temperatures: Ti_5Al_{11} and Ti_2Al_5. The phase Ti_5Al_{11} was found as a single phase in as-cast alloys of 69 to 71 at. pct Al. The homogeneity range of Ti_5Al_{11} was reported from 68.5 to 70.9 at. pct Al; this phase should transform eutectoidally into $TiAl_2$ and Ti_2Al_5 at 1206 °C. The compound Ti_2Al_5, with fixed stoichiometry, was found to exist between 1215 °C and 970 °C $< T <$ 1000 °C, where it decomposes eutectoidally into $TiAl_3$ and $TiAl_2$.

In the present work, Ti_5Al_{11} was observed in heat-treated samples at 1300 °C to 1000 °C. The homogeneity range reaches from 66 to 71 at. pct Al at 1300 °C. The axial ratio c/a of the CuAu substructure of Ti_5Al_{11} increases linearly with the aluminum content throughout the entire homogeneity range (Figure 4). The superstructure of Ti_5Al_{11} shows a long period modulation in the [001] direction of the CuAu substructure. This structural variety cannot be described completely, even with two superstructures as proposed by Schuster and Ipser.[21] These modulations are in some compositions incommensurate with the CuAu substructure. Concerning these facts, the aluminum-rich high-temperature part of the phase diagram has been characterized by a single phase showing the common CuAu substructure with linearly increasing axial ratio c/a. Below 1215 °C, (Figures 1 and 3) the homogeneity range of Ti_5Al_{11} decreases rapidly with the appearance of the phase $TiAl_2$. The eutectoidal decomposition temperature was determined to be 995 °C, in good agreement with the temperatures proposed by Loiseau *et al.*[19] and by Schuster and Ipser.[21]

Raman and Schubert[17] observed a low-temperature phase Ti_9Al_{23}, which was nearly single phase in the alloy $Ti_{28}Al_{72}$ after annealing at 730 °C for 11 days. In the phase diagram drawn by these authors,[17] the phase Ti_9Al_{23} exists up to 780 °C, where it transforms peritectoidally into $TiAl_2$ and $TiAl_3$. Van Loo and Rieck[33] found a phase called Ti_8Al_{24} after annealing a diffusion couple at 585 °C. This phase did not form at 638 °C; instead, the formation of the high-temperature modification $TiAl_3$ (h) was observed. Since that time, it has been clear that a low-temperature phase exists around $TiAl_3$, but its composition, as well as the temperature of the phase transformation, remained unclear. Loiseau *et al.*[19] reported low-temperature long period structures in alloys around 72 at. pct Al at temperatures below 900 °C. Analogical one-dimensional antiphase domain structures were observed by Miida *et al.*[34] in alloys containing 67.5 to 73.5 at. pct Al at annealing temperatures of up to about 950 °C. In the present work, it was confirmed that a low-temperature phase exists with the crystal structure described by Raman and Schubert[17] and by van Loo and Rieck.[33] The composition of this phase was determined to be the same as that of $TiAl_3$ (h), which shows a small homogeneity range. The transformation temperature is strongly dependent on the exact composition of $TiAl_3$: aluminum-rich $TiAl_3$ (l) transforms at 735 °C into $TiAl_3$ (h), whereas for titanium-rich $TiAl_3$, the transformation temperature lies as high as about 950 °C.

V. CONCLUSIONS

The phase equilibria for the aluminum-rich part of the binary system Ti-Al have been reinvestigated. Seven stable intermetallic phases and two metastable phases have been observed.

1. The aluminum-rich phase boundary of TiAl changes from 62 at. pct Al at 1300 °C to 56 at. pct Al at 800 °C.
2. The high-temperature phase $Ti_{1-x}Al_{1+x}$ exists at even lower temperatures than previously reported and decomposes eutectoidally into TiAl and $TiAl_2$ at ≈1170 °C.
3. The low-temperature phase Ti_3Al_5 is formed by a peritectoid reaction from TiAl and $TiAl_2$ at ≈810 °C.
4. The homogeneity range of the phase Ti_5Al_{11} reaches from 66 to 71 at. pct Al at 1300 °C. Ti_5Al_{11} transforms into $TiAl_2$ by a polymorphic phase transformation at 1215 °C and 66.7 at. pct Al. The eutectoidal decomposition of Ti_5Al_{11} into $TiAl_2$ and $TiAl_3$ (h) occurs at ≈995 °C and 71.5 at. pct Al.
5. The metastable phase $TiAl_2$ (m) ($ZrGa_2$ type) is observed in the as-cast alloys.
6. The phase $TiAl_3$ exists in two stable modifications: $TiAl_3$ (h) and $TiAl_3$ (l). The transformation temperature strongly depends on the exact composition of the phase within its homogeneity range.
7. The metastable phase $TiAl_3$ (m) (Cu_3Au type) is observed in liquid quenched alloys.

REFERENCES

1. D. Banerjee: in *Intermetallic Compounds, Principles and Practice*, J.H. Westbrook and R.L. Fleischer, eds., John Wiley, New York, NY, 1994, vol. 2, pp. 91-131.
2. S.C. Huang and J.C. Chesnutt: in *Intermetallic Compounds, Principles and Practice*, J.H. Westbrook and R.L. Fleischer, eds., John Wiley, New York, NY, 1994, pp. 73-90.
3. H. Clemens and F. Jeglitsch: *Prakt. Metallogr.*, 2000, vol. 37, pp. 194-217.
4. D. Veeraraghavan, U. Pilchowski, B. Natarajan, and V.K. Vasudevan: *Acta Mater.*, 1998, vol. 46, pp. 405-21.
5. J.J. Ding, G.W. Qin, S.M. Hao, X.T. Wang, and G.L. Chen: *J. Phase Equilibria*, 1996, vol. 17, pp. 117-20.
6. R. Kainuma, M. Palm, and G. Inden: *Intermetallics*, 1994, vol. 2, pp. 321-32.
7. S.A. Jones and M.J. Kaufman: *Acta Metall. Mater.*, 1993, vol. 41, pp. 387-98.
8. A. Hellwig, G. Inden, and M. Palm: *Scripta Metall. Mater.*, 1992, vol. 27, pp. 143-48.
9. S.C. Huang and P.A. Siemers: *Metall. Trans. A*, 1989, vol. 20A, pp. 1899-1906.
10. J.C. Mishurda, J.C. Lin, Y.A. Chang, and J.H. Perepezko: in *High Temperature Ordered Intermetallic Alloys III*, Materials Research Society Symposia Proceedings, C.T. Liu, A.I. Taub, N.S. Stoloff, and C.C. Koch, eds., Materials Research Society, Pittsburgh, PA, 1989, vol. 133, pp. 57-62.
11. C. McCullough, J.J. Valencia, C.G. Levi, and R. Mehrabian: *Acta Metall.*, 1989, vol. 37, pp. 1321-36.
12. R.D. Shull, A.J. McAlister, and R.C. Reno: in *Proc. 5th Int. Conf. on Titanium*, Munich, 1984, G. Lütjering, U. Zwicker, and W. Bunk, eds., Deutsche Gesellschaft für Metallkunde, Oberursel, 1985, pp. 1459-66.
13. E.W. Collings: *Metall. Trans. A*, 1979, vol. 10A, pp. 463-74.
14. H.R. Ogden, D.J. Maykuth, W.L. Finlay, and R.I. Jaffee: *Trans. AIME*, 1951, vol. 191, pp. 1150-55.
15. E.S. Bumps, H.D. Kessler, and M. Hansen: *Trans. AIME*, 1952, vol. 194, pp. 609-14.
16. M. Pötzschke and K. Schubert: *Z. Metallkd.*, 1962, vol. 53, pp. 548-61.
17. A. Raman and K. Schubert: *Z. Metallkd.*, 1965, vol. 56, pp. 44-52.
18. A. Loiseau and C. Vannuffel: *Phys. Status Solidi (a)*, 1988, vol. 107, pp. 655-71.
19. A. Loiseau, G. van Tendeloo, R. Portier, and F. Ducastelle: *J. Phys.*, 1985, vol. 46, pp. 595-613.
20. K. Kaltenbach, S. Gama, D.G. Pinatti, and K. Schulze: *Z. Metallkd.*, 1989, vol. 80, pp. 511-14.
21. J.C. Schuster and H. Ipser: *Z. Metallkd.*, 1990, vol. 81, pp. 389-96.
22. J.L. Murray: *Metall. Trans. A*, 1988, vol. 19A, pp. 243-47.
23. U.R. Kattner, J.-C. Lin, and Y.A. Chang: *Metall. Trans. A*, 1992, vol. 23A, pp. 2081-90.

24. F. Zhang, S.L. Chen, Y.A. Chang, and U.R. Kattner: *Intermetallics*, 1997, vol. 5, pp. 471-82.
25. J.G. Costa Neto, S. Gama, and C.A. Ribeiro: *J. Alloys Compounds*, 1992, vol. 182, pp. 271-80.
26. J. Braun, M. Ellner, and B. Predel: *Z. Metallkd.*, 1994, vol. 85, pp. 855-62.
27. J. Cissé, H.W. Kerr, and G.F. Bolling: *Metall. Trans.*, 1974, vol. 5, pp. 633-41.
28. J. Braun, M. Ellner, and B. Predel: *Z. Metallkd.*, 1995, vol. 86, pp. 870-76.
29. J. Braun, M. Ellner, and B. Predel: *J. Alloys Compounds*, 1994, vol. 203, pp. 189-93.
30. R. Miida: *Jpn. J. Appl. Phys.*, 1986, vol. 25, pp. 1815-24.
31. R. Miida, S. Hashimoto, and D. Watanabe: *Jpn. J. Appl. Phys.*, 1982, vol. 21, pp. L59-L61.
32. J. Braun and M. Ellner: *J. Alloys Compounds*, 2000, vol. 309, pp. 118-122.
33. F.J.J. van Loo and G.D. Rieck: *Acta Metall.*, 1973, vol. 21, pp. 61-71 and 73-84.
34. R. Miida, M. Kasahara, and D. Watanabe: *Jpn. J. Appl. Phys.*, 1980, vol. 19, pp. L707-L710.