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Investigation of the Al-Ti-Pt alloy system at 1100 °C

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ABSTRACT

The 1100 °C isothermal section of the Al–Ti–Pt system was experimentally studied in the compositional region below 50 at.% Pt. Most of the binary Al–Ti and Al–Pt intermetallics dissolve about 1.5–3.5 at.% of the third element. Only TiAl and Ti₃Al contain up to ~5.5 at.% Pt and Al₂Pt ~13 at.% Ti. The Ti₃Pt, Ti₃Pt₄ and TiPt phases extend up to 7.5, 9 and 30 at.% Al, respectively. The homogeneity range of the ternary phase τ_1 extends from Al_{63.3}Ti_{30.6}Pt_{6.1} to Al_{69.0}Ti_{24.2}Pt_{6.6} and that of τ_2 from Al_{44.1}Ti_{34.0}Pt_{21.9} to Al_{55.1}Ti_{20.9}Pt_{24.0}. The τ_3 -phase is formed in the compositional region from Al₃₇Ti_{37.5}Pt_{25.5} to Al₄₂Ti₃₂Pt₂₆. Only the Nb(Ir,Al)₂-type structure of the latter was revealed. The τ_4 -phase exists between Al_{31.3}Ti_{3.7}Pt_{3.5} and Al_{36.6}Ti_{29.4}Pt_{3.4} while the τ_5 -phase exists between Al_{12.9}Ti_{58.9}Pt_{28.2} and Al_{27.3}Ti_{57.3}Pt_{1.5.4}. Apart from these previously reported phases, five new ternary compounds designated τ_6 to τ_{10} were revealed. The τ_6 -phase exists between the Al_{32.5}Ti_{54.2}Pt_{20.3} and the Al₃₀Ti₅₄Pt₁₆ compositions, and probably has a primitive cubic structure with *a* = 0.68477(6) nm. The τ_7 -phase was found to be formed around the Al₁₂Ti₅₁Pt₃₇ composition, τ_8 , τ_9 and τ_{10} -phases exist in the compositional ranges of Al_{28.5}Ti₅₅Pt_{27.5} to Al_{33.7}Ti₄₀Pt_{26.3}, Al_{34.5}Ti₄₈Pt_{17.5} to Al₃₈Ti₄₄Pt₁₈ and Al_{32.6}Ti_{44.3}Pt_{23.1} to Al_{37.4}Ti₄₁Pt_{21.6}, respectively.

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1. Introduction

The Al–Ti–Pt alloy system was experimentally studied in Refs. [1,2] at 950 °C in a compositional region adjacent to the Al–Ti terminal. Several contributions were also devoted to individual ternary Al–Ti–Pt phases [2–4]. This alloy system is related to the Al–Ti–Pd alloy system, also studied in Refs. [1,2] at 950 °C and more recently in Ref. [5] at 930 and 1100 °C.

Five ternary phases designated τ_1 to τ_5 were reported in Refs. [1–5] (see Table 1 for structural details). The τ_1 -phase and τ_2 -phase were found to be formed around the Al₆₇Ti₂₆Pt₇ and Al₅₀Ti₂₅Pt₂₅ compositions, respectively. In Ref. [1] the τ_3 -phase was associated with the Al₄₂Ti₄₄Pt₁₄ composition and in Ref. [2] with the Al_{43.2}Ti_{37.8}Pt₁₉ composition. The structural variant of this phase designated τ'_3 in the following was found to exist around 25 at.% Pt and 33.5–36 at.% Ti [2]. The τ_4 -phase is formed around the equiatomic composition AlTiPt, while the τ_5 -phase is formed in a compositional range between Al₁₄Ti₅₈Pt₂₈ and Al₂₁Ti₆₃Pt₁₆. The solubility of Pt in binary titanium aluminides was found to be in the order of 2.5 at.%.

The phase equilibria presented in Refs. [1,2] are quite schematic and some details are controversial. Even binary boundary alloy systems Al–Pt, Al–Ti and Ti–Pt are still insufficiently well established. In the present work the Al–Ti–Pt phase diagram was studied at 1100 °C in the compositional region below 50 at.% Pt. We selected the temperature higher than that applied in Refs. [1,2] in order to improve the equilibration of the studied alloys. The information on the Al–Pt phase diagram is taken from Refs. [6,7] and on the Ti–Pt phase diagram from Refs. [8–10]. The extensively studied Al–Ti constitutional diagram is still under discussion (see Refs. [11–13] and references therein). As mentioned in Ref. [5] and also applicable here, both diagrams in Refs. [12,13] are consistent in the temperature range relevant to our study. The corresponding data are accepted in the following.

The constitutions of the Al–Ti–Pt and Al–Ti–Pd alloy systems will be compared.

2. Experimental

The starting materials were Al of 99.995 mass%, Ti of 99.98 mass% and Pt of 99.8 mass% purity. Ternary alloys (2.5-3 g) of more than 60 compositions were prepared by either arc melting or levitation inductive melting under an argon atmosphere. They were subsequently annealed under an argon atmosphere at $1100 \degree$ C for 72–209 h and water quenched.

The alloys were studied by scanning electron microscopy (SEM) and powder Xray diffraction (XRD). The compositions of the phases were determined in SEM by energy dispersive X-ray analysis (EDX) on polished unetched cross sections. XRD was

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Table 1

Crystallographic data of the Al-Ti-Pt phases in the studied compositional and temperature ranges. The literature data are given with the corresponding references.

Phase	Space group	Prototype	Lattice parameters, nm			Comment	
			a	b	С		
h-TiPt (β)	PmĪm	CsCl	0.3192	-	-	[15]	
l-TiPt	Pmma	AuCd	0.455	0.273	0.479	[15]	
			0.4592	0.2761	0.4838	[16]	
Ti₃Pt	PmĪn	Cr ₃ Si	0.50327	-	-	[17]	
			0.5030	-	-	[18]	
Ti ₄ Pt ₃	Unknown	-	-	-	-	[10]	
β-AlPt	Pm3m	CsCl	0.3125	-	-	[19]	
α-AlPt	P213	FeSi	0.4864	-	-	[20]	
Al_3Pt_2	P3m1	Al ₃ Ni ₂	0.4204	-	0.5171	[21]	
Al ₂ Pt	Fm3m	CaF ₂	0.5910	-	-	[21] Al ₆₇ Pt ₃₃	
			0.5920	-	-	[21] Al ₆₈ Pt ₃₂	
Al ₂₁ Pt ₈	I4 ₁ /a	Al ₂₁ Pt ₈	1.2964	-	1.0684	[21]	
α	PG_3/mmc	Mg	0.2951	-	0.4684	[22]	
α2	$P6_3/mmc$	Ni ₃ Sn	0.5775	-	0.4655	[23]	
γ	P4/mmm	AuCu	0.4001	-	0.4071	[23]	
η	I4 ₁ /amd	HfGa ₂	0.3976	-	2.436	[23]	
ζ	P4/mmm	Ti ₂ Al ₅	0.39053	-	2.91963	[24]	
ε	I4/mmm	TiAl ₃	0.3846	-	0.8594	[23]	
τ_1	Fm3m	Cu	0.39577(1)	-	-	[1], 950 °C, Al ₆₅ Ti ₂₅ Pt ₁₀	
	Pm3m	AuCu ₃	0.396245(3)	-	-	[3], 950 °C, Al ₆₈ Ti ₂₆ Pt ₆	
τ_2	Fm3m	Th_6Mn_{23+1}	1.21921(1)	-	-	[1], 950 °C, Al ₅₀ Ti ₂₅ Pt ₂₅	
			1.22315(5)	-	-	[3], as-cast, Al ₅₀ Ti ₂₅ Pt ₂₅	
τ3	$P6_3/mmc$	MgZn ₂	0.51309(1)	-	0.82691(1)	[1], 950 °C, Al _{42,3} Ti _{44,1} Pt _{13,6}	
τ'_2	P6 ₃ /mcm	Nb(Ir,Al)2	0.89014(3)	-	0.82019(3)	[2], as-cast, Al _{39,6} Ti _{36,0} Pt _{24,4}	
2			0.88994(4)	-	0.81974(3)	[2] 950 °C, Al _{40,0} Ti _{34,9} Pt _{25,1}	
τ_4	P6 ₃ /mmc	ZrBeSi	0.43908(9)	-	0.54823(10)	[4], 1100 °C, Al _{33,4} Ti _{33,3} Pt _{33,3}	
			0.43964(2)		0.54868(3)	[2], 950 °C, Al _{33,4} Ti _{33,3} Pt _{33,3}	
τ5	$P4_2nm$ or $P\overline{4}n2$ or $P4_2/mnm$		0.97019(20)	_	0.50231(13)	[4], 1100 °C, Al ₁₅ Ti ₆₀ Pt ₂₅	
τ ₆	Cubic	-	0.68477(6)	_	-	this work	
τ_7	Unknown		?			this work	
τ_8	Unknown		?			this work	
τ ₉	Unknown		?			this work	
τ_{10}	Unknown		?			this work	

carried out in transmission mode using Cu $K_{\alpha 1}$ radiation and image plate detector $(2\theta$ range: 5–120°).

3. Results and discussion

3.1. Binary phases

According to Ref. [8], at 1100 °C β -Ti can dissolve up to 10 at.% Pt and the high-Ti part of the Ti–Pt alloy system also contains intermetallic phases Ti₃Pt and h-TiPt (see Table 1) exhibiting some compositional ranges. One more phase of unknown structure designated Ti₄Pt₃ was reported in Ref. [9]. It was found to exist between 41.7 and 43.4 at.% Ti below 1205 °C. The temperature of the transition between high-temperature h-TiPt and low-temperature l-TiPt varies between 980 and 1050 °C depending on the composition [8–10], i.e. not much below the temperature of 1100 °C applied for our ternary samples. Powder XRD analysis of the relevant ternary samples annealed at and quenched from 1100 °C indicated the presence of some l-TiPt together with h-TiPt. It can be explained rather by transformation by cooling than by increase of the transition temperature between these phases due to the addition of Al.

In our experiments a sample of composition $Ti_{57.2}Pt_{42.8}$ annealed at 1100 °C exhibited a major phase associated with Ti_4Pt_3 of Ref. [9]. Powder XRD pattern obtained from this sample was qualitatively similar to that in Fig. 6 of Ref. [9]. Investigation of the samples by transmission electron microscopy revealed strongly faulted microstructure [14]. This did not allow the structural analysis of this phase also by electron diffraction.

Table 2

Diffraction data of the τ_6 -phase (Cubic, $a = 0.68477(6)$ nm, average $\Delta 2\theta = 0.02$	0°,
maximum $\Delta 2\theta = 0.134^{\circ}$, figure of merit F(30) = 49.9. From the total of 50 collect	ed
reflections, those below 3% are not included).	

chections, those below 5% are not included).										
No.	h	k	1	$d_{\rm obs}$	d_{calc}	I/I_0				
1	1	1	0	0.48506	0.48421	29				
2	1	1	1	0.39589	0.39535	50				
3	2	0	0	0.34259	0.34239	25				
4	2	1	0	0.30625	0.30624	39				
5	2	1	1	0.27969	0.27956	12				
6	2	2	0	0.24217	0.24210	9				
7	3	0	0	0.22828	0.22826	100				
8	3	1	0	0.21652	0.21654	65				
9	3	1	1	0.20643	0.20647	23				
10	2	2	2	0.19773	0.19768	3				
11	3	2	0	0.18989	0.18992	11				
12	3	2	1	0.18300	0.18301	36				
13	4	1	0	0.16610	0.16608	19				
14	3	3	0	0.16139	0.16140	5				
15	3	3	1	0.15709	0.15710	5				
16	4	2	0	0.15308	0.15312	3				
17	4	2	1	0.14945	0.14943	6				
18	4	2	2	0.13974	0.13978	6				
19	5	0	0	0.13694	0.13695	6				
20	5	1	0	0.13429	0.13429	31				
21	5	1	1	0.13178	0.13178	9				
22	5	2	0	0.12716	0.12716	20				
23	5	2	1	0.12501	0.12502	7				
24	5	3	1	0.11576	0.11575	4				
25	6	0	0	0.11413	0.11413	9				
26	5	4	0	0.10694	0.10694	6				
27	5	4	1	0.10565	0.10566	3				
28	5	3	3	0.10442	0.10443	3				
29	6	3	0	0.10206	0.10208	4				
30	6	3	1	0.10096	0.10096	3				
31	7	0	0	0.09780	0.09782	3				

The Ti_3Pt and Ti_3Pt_4 phases dissolve 7.5 and 9 at.% Al, respectively, while TiPt dissolves up to 30 at.% Al.

At the studied temperature the relevant part of the Al–Pt alloy system contains the congruent AlPt and Al_3Pt_2 phases and peritectically forming Al_2Pt and $Al_{21}Pt_8$ phases [6,7] (see Table 1). Only in Al_2Pt does the solubility of Ti reach 13 at.%; the other Al–Pt phases were found to dissolve no more than 3.5 at.% Ti.

At 1100 °C the Al–Ti system contains the terminal solid solutions α_{Ti} and β_{Ti} , and intermediate phases α_2 (AlTi₃), γ (AlTi), η (Al₂Ti), ζ (Al₅Ti₂) and high-temperature ϵ (Al₃Ti) (see Table 1 for crystallographic data). The β_{Ti} -phase extends up to ~20 at.% Al, α_2 between 27 and 38 at.% Al, γ between 47 and 61 at.% Al. The other phases exhibit narrower compositional regions. The solubility of Pt in the Al–Ti intermetallics is quite low. The TiAl₃, Ti₂Al₅ and TiAl₂ phases dissolve up to 1.5 at.% Pt, whereas TiAl and Ti₃Al contain up to ~5.5 at.% Pt.

The observed propagation of the binary phases into the ternary space is exhibited in the isothermal section (see below).

3.2. Ternary phases

Apart from the ternary phases mentioned in the Introduction, our study revealed five more ternary phases designated τ_6 , to τ_{10} . Their compositions were determined in two-phase and three-phase equilibrated samples and new samples were produced in order to reduce the volume fraction of impurity phases. The powder XRD patterns of the essentially major τ_6 , τ_7 , τ_8 and τ_9 phases selected after SEM/EDX examinations are shown in Fig. 1 together with those of the τ_1 to τ_5 . The XRD diffraction pattern of τ_{10} has not been obtained due to absence of a sample contained major fraction of this phase. The diffraction pattern of the τ_6 -phase could be indexed for a primitive cubic structure with the lattice parameter a = 0.68477(6) nm (see Table 2). The possible lattice constants of the τ_7 , τ_8 , τ_9 and τ_{10} -phases exhibiting complicated diffraction patterns were not determined.

According to our measurements, the τ_1 -phase exists between the $Al_{63.3}Ti_{30.6}Pt_{6.1}$ and the $Al_{69.0}Ti_{24.2}Pt_{6.6}$ compositions, the τ_2 -phase between the $Al_{44.1}Ti_{34.0}Pt_{21.9}$ and the $Al_{55.1}Ti_{20.9}Pt_{24.0}$ compositions and the τ_3 -phase in a small compositional region from $Al_{37}Ti_{37.5}Pt_{25.5}$ to $Al_{42}Ti_{32}Pt_{26}$. Only the τ_3' superstructure (see Table 1) was revealed in our experiments at 1100 °C.

The compositional regions between Al_{31.3}Ti_{33.7}Pt₃₅ and Al_{36.6}Ti_{29.4}Pt₃₄ were determined for the τ_4 -phase and from Al_{12.9}Ti_{58.9}Pt_{28.2} to Al_{27.3}Ti_{57.3}Pt_{15.4} for the τ_5 -phase. The τ_6 -phase exists between the Al_{25.5}Ti_{54.2}Pt_{20.3} and the Al₃₀Ti₅₄Pt₁₆ compositions. The τ_7 -phase occupies a small range around the Al₁₂Ti₅₁Pt₃₇ composition, while the τ_8 , τ_9 and τ_{10} -phases are formed in the compositional ranges of Al_{28.5}Ti₅₅Pt_{27.5} to Al_{33.7}Ti₄₀Pt_{26.3}, Al_{34.5}Ti₄₈Pt_{17.5} to Al₃₈Ti₄₄Pt₁₈ and Al_{32.6}Ti_{44.3}Pt_{23.1} to Al_{37.4}Ti₄₁Pt_{21.6}, respectively.

The absence of the τ_7 -phase in the as-cast samples and the existence of the $\tau_7 + Ti_3Pt_5 + \tau_4$, $\tau_7 + \tau_4 + Ti_3Pt_5$ and $Ti_3Pt + \tau_7 + \tau_4$ equilibria at 1100 °C probably indicate a peritectoid character of its formation at temperatures above 1100 °C.

3.3. Isothermal section 1100°C

The partial 1100 °C isothermal section of the Al–Ti–Pt alloy system determined in our work is shown in Fig. 2. The equiatomic τ_4 -phase is in equilibrium with the τ_2 , τ_3 , τ_5 , τ_7 and τ_8 -phases and the ternary extensions of the binary



Fig. 1. Powder XRD patterns of the alloys annealed at 1100 °C (CuK_{\alpha1} radiation, the corresponding phases are mentioned in brackets): (a) Al_{67,4}Ti_{24,8}Pt_{7,8} ($\tau_1 + Al_2Pt^*$), (b) Al_{56,4}Ti₃₀Pt_{13.6} (τ_2 and some γ whose reflections are marked by arrows), (c) Al_{35,8}Ti_{37,8}Pt_{26,4} ($\tau'_3 + \tau^*_8$), (d) Al_{34,7}Ti_{29,6}Pt_{35,7} (τ_4), (e) Al_{16,9}Ti_{57,6}Pt_{25,5} ($\tau_5 + \tau^*_6 + \tau^*_8$), (f) Al₃₀Ti_{50,8}Pt_{19,2} ($\tau_6 + \tau^*_{10}$), (g) Al_{13,9}Ti_{49,4}Pt_{36,7} ($\tau_7 + \tau^*_4 + Ti_4Pt^*_3$), (h) Al_{32,1}Ti_{43,2}Pt_{24,7} ($\tau_8 + \tau^*_{10}$) and (j) Al_{38,1}Ti_{44,1}Pt_{17,8} ($\tau_9 + \tau^*_{10}$). The additional phases marked by (*) were observed by SEM in very small amounts whose contributions to the powder XRD patterns were essentially minor.

phases Ti₄Pt₃, TiPt, Al₃Pt₂ and Al₂Pt. The three-phase equilibria τ_4 +TiPt+Al₃Pt₂, τ_4 +Al₃Pt₂+Al₂Pt, τ_4 +Al₂Pt+ τ_2 , τ_2 + τ_3 + τ_4 , τ_3 + τ_4 + τ_8 , τ_4 + τ_5 + τ_8 , τ_4 +Ti₃Pt+ τ_5 , τ_4 +Ti₃Pt+ τ_7 , τ_4 +Ti₄Pt₃+ τ_7 and τ_4 +Ti₄Pt₃+TiPt were established. Ternary phases, excluding τ_3 , τ_7 , τ_8 and τ_{10} , coexist in equilibria with the Al–Ti binaries. Thus, the τ_5 +Ti₃Pt+ α , τ_5 + α + α_2 , τ_5 + τ_6 + α_2 , τ_6 + τ_9 + α_2 , τ_9 + α_2 + γ , τ_9 + τ_2 + γ , τ_1 + τ_2 + γ , τ_1 +Al₂Pt+ ε equilibria were revealed. The equilibrium of the τ_1 -phase with η and ζ phase was concluded on the basis of the investigation of two-



Fig. 2. Partial 1100 °C isothermal section of Al–Ti–Pt. The liquid is designated L. The compositions of the studied samples are shown by symbols explained in the drawing. Provisional tie-lines are shown by broken lines.

phase and neighboring three-phase samples. Moreover, the τ_2 , τ_3 , τ_6 , τ_8 , τ_9 and τ_{10} -phases coexist in equilibria with each other.

Three-phase equilibria involving the liquid phase include ε + Al₂Pt + L and Al₂Pt + Al₂1Pt₈ + L.

The compositional regions of the ternary phases determined in Refs. [1,2] are compared with our findings in Fig. 3. The results in Ref. [2] are in fair agreement with our isothermal section, while the composition of the τ_3 -phase in Ref. [1] does not correspond to any single-phase region in either Ref. [2] or our work. Subsequently, the $\tau_2 + \tau_3 + \gamma$ and $\tau_3 + \alpha_2 + \gamma$ equilibria reported in Ref. [1] were not confirmed and the τ_3 phase was not found in equilibrium with the binary Al–Ti phases.

3.4. Comparison with Al-Ti-Pd

The compositional regions of the phases in the Al–Ti–Pt alloy system are compared in Fig. 4 with those determined in Ref. [5] in the Al–Ti–Pd alloy system at the same 1100 °C. Also the composition of the Al–Ti–Pd τ_2 -phase forming somewhat below this

temperature is added. The solubility of Pt and Pd in the Al–Ti binary phases is comparable. The three ternary compounds revealed in Al–Ti–Pd were also found in Al–Ti–Pt. They are designated by the same names. Their compositional regions are somewhat different (see Fig. 4). Both the MgZn₂-type structure of the τ_3 -phase and the Nb(Ir,Al)₂-type superstructure variants (designated τ'_3) were observed in the Al–Ti–Pd alloy system. The MgZn₂-type structure, reported in Ref. [1] to be also formed in Al–Ti–Pt at 930 °C, was not observed in our study at 1100 °C nor in Ref. [2] at 930 °C.

The main differences between the constitutions of the Al–Ti–Pd and Al–Ti–Pt alloy systems are due to the differences between the Al–Pd and the Al–Pt binary systems. Instead of a wide continuous region of the β solid solution in the former, the disordered β_{Ti} solid solution only slightly extends into the ternary compositional region in the latter, and the ordered solid-solution β extends from TiPt as a narrow stripe towards AlPt. In the ternary region corresponding in Al–Ti–Pd to the β -phase numerous ternary phases were revealed in Al–Ti–Pt. In total the number of ternary phases in the Al–Ti–Pt system is much higher than in Al–Ti–Pd.



Fig. 3. The results of the present study as in Fig. 2 (thin solid lines) compared to those in Ref. [1] (red in the online version) and Ref. [2] (blue in the online version). The literature data correspond to 950 °C.



Fig. 4. Compositional regions of the phases in Al–Ti–Pt (pink in the online version) compared to those in Al–Ti–Pd [5]. The tie-lines correspond to the equilibrium in Al–Ti–Pd at 1100 °C. The Al–Ti–Pd τ_2 -phase forming at lower temperatures is also shown.

4. Conclusions

Partial isothermal section of the Al–Ti–Pt phase diagram at $1100 \,^{\circ}$ C was determined in the compositional region below 50 at.% Pt.

Binary Al–Ti phases dissolve from 1.5 to 5.5 at.% Pt. The solubility of Ti in Al₂Pt reaches 13 at.%, and the other Al–Pt phases forming in the studied compositional region dissolve below 3.5 at.% of Ti. The TiPt phase extends up to 30 at.% Al, Ti₃Pt and Ti₃Pt₄ up to 7.5 and 9 at.% Al, respectively.

The ternary compounds τ_1 to τ_5 earlier reported were confirmed. The MgZn₂-type structure associated in the literature with the τ_3 -phase was not found at 1100 °C, but only its superstructure of the Nb(Ir,Al)₂ type.

Five regions of the new ternary phases, designated τ_6 , to τ_{10} were revealed. The structures of these phases have not yet been determined. The τ_6 -phase probably has a primitive cubic structure with the lattice parameter *a* = 0.68477 nm.

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