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An investigation of the high-Al part of the Al–Pd–Ru phase diagram at 1000 and 1100 ºC

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Partial isothermal sections of the Al–Pd–Ru phase diagram at 1000 and 1100°C are presented. The Al–Pd orthorhombic ε-phases dissolve up to ~15.5 at.% Ru, $Al_{13}Ru_4$ <2.5 at.% Pd and Al_2Ru up to 1 at.% Pd. Between 65 and 80 at.% of Al ternary quasiperiodic icosahedral phase and four cubic phases were revealed. An additional complex cubic structure with a ≈ 3.96 nm was found to be formed at compositions close to those of the icosahedral phase.

Intermetallics / X-ray diffraction / Phase diagram

Introduction

Al–Pd–Ru belongs to a group of alloy systems exhibiting the formation of quasicrystals and related complex periodic intermetallics. According to the position of Ru in the periodic table this alloy system is linked to the recently studied Al–Pd–Fe [1-3] and Al–Ni–Ru [4,5].

The literature data on the Al–Pd–Ru alloy system are poor and limited to information on several individual phases. Earlier the formation of a cubic phase (P23; a = 1.5540 nm) was reported in this alloy system at $Al_{68}Pd_{20}Ru_{12}$ [6]. Another cubic phase ($Fm\bar{3}$; a = 1.56058 nm) was revealed at $Al_{66.8}Pd_{21.2}Ru_{12.0}$ [7] and one more (so-called (2/1) approximant with a = 2.0 nm) around $Al_{71}Pd_{19}Ru_{10}$ [8]. An icosahedral (I) quasicrystalline phase was found to be stable in the alloy $Al_{72}Pd_{17}Ru_{11}$ [9].

In the present contribution we report the preliminary investigation of the phases and phase equilibrium in Al–Pd–Ru in the Al–AlPd–Al_2Ru compositional triangle and the temperature range of 1000 to 1100 °C. The boundary Al–Pd phase diagram is accepted according to [10] and Al–Ru according to [11].

Experimental

Alloys were produced from the constituent elements by levitation induction melting in a water-cooled copper crucible under an Ar atmosphere. The purity of Al was 99.999%, of Pd 99.95% and of Ru 99.9%. The ingots were typically of about 5 g. The samples were re-melted again if after inspection residual Ru was detected in the broken ingots. Parts of the samples were annealed under an Ar atmosphere or vacuum for 24 to 200 h.

Single-phase samples were selected using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). Their compositions were examined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and by energy-dispersive X-ray analysis (EDX) in SEM. Powder XRD was carried out in the transmission mode using Cu $K_{\alpha 1}$ radiation and a position-sensitive detector. The samples were also studied by electron diffraction in a transmission electron microscope (TEM) operated at 200 kV. The TEM samples were powders spread on Cu grids covered by carbon films. The melting temperatures of the phases were determined by differential thermal analysis (DTA) at rates of 5 to 20 °C/min.

Results and discussion

Intermediate phases

The above-mentioned temperature and compositional range includes the binary Al–Ru intermediate phases M-$Al_{13}Ru_4$ and Al_2Ru (see Table 1). Of the Al–Pd binary phases, only AlPd is solid above 1000 ºC. Isostructural congruent AlPd and AlRu (probably) form a continuous range of solid solutions naturally separating the high-Al region of Al–Pd–Ru. This has not yet been studied due to

Table 1 Crystallographic data of the Al–Pd–Ru phases mentioned in the text. The lattice parameters are given for the compositions indicated.

Phase	S.G. or crystal symmetry	Lattice parameters				For composition
		a, nm	*b*, nm	*c*, nm	*β*, °	
M-$Al_{13}Ru_4$	*C*2/*m*	1.5862	0.8188	1.2736	107.77	
Al_2Ru	*Fddd*	0.8012	0.4717	0.8785	-	
β (AlPd)	$Pm\bar{3}m$	0.3036	-	-	-	
C	$Pm\bar{3}$	0.77568(3)	-	-	-	$Al_{74.4}Pd_{7.5}Ru_{18.1}$
C_1	$Im\bar{3}$	1. 55362(14)	-	-	-	$Al_{71.0}Pd_{12.5}Ru_{16.5}$
C_2	$Fm\bar{3}$	1.55659(2)	-	-	-	$Al_{67.7}Pd_{19.7}Ru_{12.6}$
F	*fcc*	~3.97	-	-	-	
ε	*orthorh.*	~2.35	~1.68	var.[a]		

[a] The structural variants designated ε_6 and ε_{28}, typical of binary Al–Pd, have $c \approx 1.23$ nm and $c \approx 5.70$ nm, respectively [10], in regular ε_{16} $c \approx 3.24$ nm. A transient structure observed around $Al_{76.5}Pd_{8.5}Ru_{15}$ resembles ε_{16} but several reflections were split.

difficulties in the equilibration of the relevant samples. For this reason the range around the Al_3Ru_2 phase was also excluded from our study. The M-$Al_{13}Ru_4$ and Al_2Ru phases were found to dissolve only a little of Pd: $Al_{13}Ru_4$ <2.5 at.%, Al_2Ru up to 1 at.%.

The Al–Pd ε-phases are solid below 790 °C [10], but with the increase of the Ru concentration this temperature increases, reaching 1030 °C at ~15.5 at.% Ru. Therefore this phase already appears in the 1000 °C isothermal section (see below) in a ternary range separated from the Al–Pd terminal. The continuity of this range was confirmed by investigation of intermediate alloys at lower temperatures and by diffraction examinations. Similarly to the structure typical of other Al–Pd–TM alloy systems [12,13], the structures observed in ternary alloys belonging to the ε-range exhibited variations. Around the $Al_{76.5}Pd_{8.5}Ru_{15}$ composition, i.e. close to its high-Ru limit, transient structures resembling ε_{16} were revealed by electron diffraction. A more detailed description of these structures is given in [13].

Three cubic phases isostructural to the Al–Pd–Fe C, C_1 and C_2 phases were revealed in Al–Pd–Ru. They are designated below in the same way. The electron diffraction patterns of these phases along the [110] directions are compared in Fig. 1. In addition, also the cubic "2/1 approximant" phase described in [8] was observed in our experiments but it is formed below 1000ºC. On the other hand, the existence of the cubic phase reported in [6] was not confirmed.

The primitive cubic C-phase ($Pm\bar{3}$) is formed in a compositional range between about $Al_{73.0}Pd_{5.0}Ru_{22}$ and $Al_{70.5}Pd_{15.0}Ru_{14.5}$. Its powder XRD pattern is shown in Fig. 2a. The refined lattice parameter was $a = 0.77568(3)$ nm for the $Al_{74.4}Pd_{7.5}Ru_{18.1}$ composition. The highest melting temperature of C is ~1300 ºC.

The body-centered cubic C_1-phase ($Im\bar{3}$) was formed below 1000°C. The single-phase sample of C_1 has not yet been obtained. The refinement of its lattice parameter was done using the diffraction data from a sample annealed at 900 °C containing some Al_2Ru. The value of $a = 1.5532(4)$ nm was obtained for $Al_{71.0}Pd_{12.5}Ru_{16.5}$. The lattice parameter of the C_1-phase is twice as large as that of the C-phase.

The diffraction reflections typical of the C_1-phase were also observed in samples of $Al_{71.0}Pd_{12.5}Ru_{16.5}$

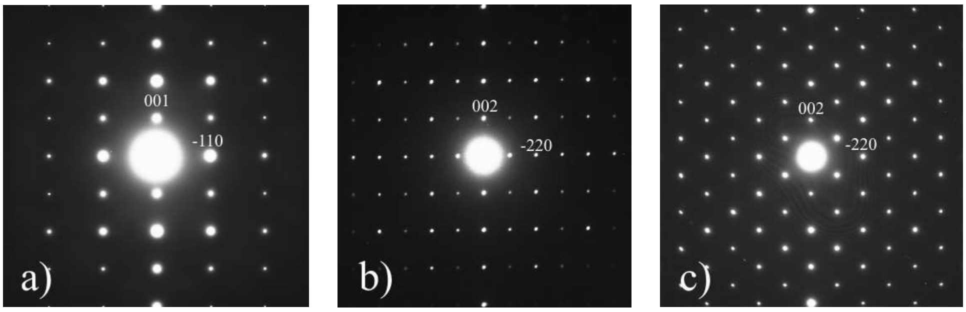

Fig. 1 Electron diffraction patterns, Z.A. = [110] of the cubic phases: a) C, b) C_1 and c) C_2.

and close compositions annealed at 1000 ºC, but this was associated with transformations occurring during cooling.

The face-centered cubic C_2-phase ($Fm\bar{3}$) is formed in a wide compositional range between about $Al_{70}Pd_{15}Ru_{15}$ and $Al_{67}Pd_{24}Ru_{9}$. Its powder XRD pattern (Fig. 2b) was indexed using a = 1.55659(5) nm for the $Al_{67.7}Pd_{19.7}Ru_{12.6}$ composition. The highest melting temperature of C_2 is 1184 ºC.

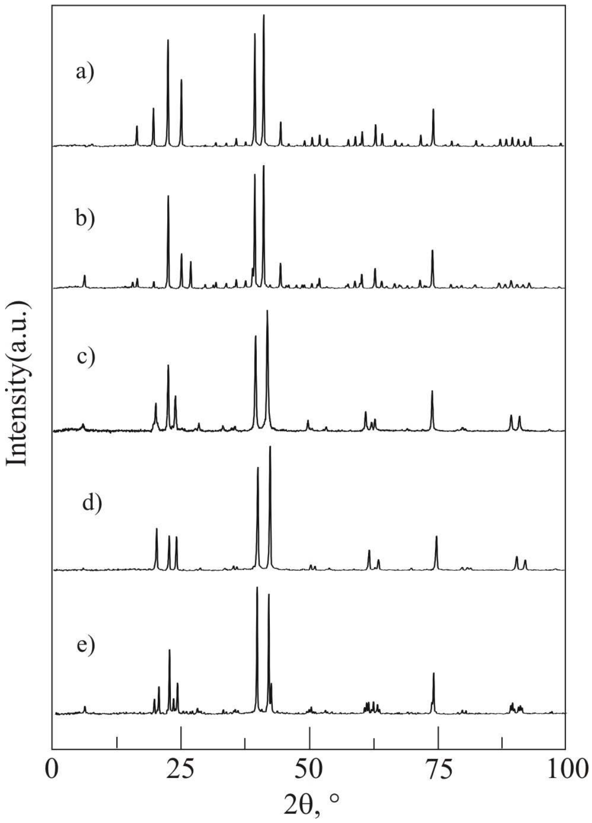

Fig. 2 Powder XRD patterns (Cu $K_{\alpha1}$ radiation) of the: a) C-phase, b) C_2-phase, c) I-phase, d) I-phase of $Al_{64.3}Cu_{23.3}Ru_{12.4}$ [14] and e) F-phase.

The stability of the ternary icosahedral quasicrystalline phase (I-phase) was confirmed. The I-phase is formed in a compositional range between ~$Al_{72.5}Pd_{13}Ru_{14.5}$ and $Al_{70.0}Pd_{19.5}Ru_{10.5}$. The highest melting temperature of I is 1080ºC. It is isostructural to other stable I-phases in ternary alloy systems of Al with transition metals. The powder XRD pattern of the Al–Pd–Ru I-phase (Fig. 2c) is very similar to that of the Al–Cu–Ru I-phase published in [14] (see Fig. 2d for the $Al_{64.3}Cu_{23.3}Ru_{12.4}$ composition). The electron diffraction pattern along the 5-fold zone axis is shown in Fig. 3b

A face-centered cubic phase with a ≈ 3.96 nm was revealed close to the I-region around composition $Al_{72.5}Pd_{13.0}Ru_{14.5}$. In the following it is designated F-phase. The electron diffraction pattern along the [110] zone axis is shown in Fig. 3a. Its XRD pattern (Fig. 2e) shows a close structural relation to the I-phase. Due to such a large unit cell the reliable indexation of the powder XRD pattern is difficult and not yet complete.

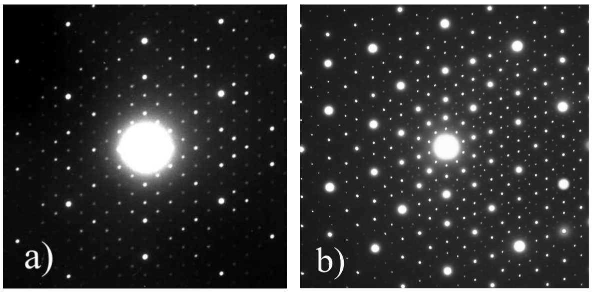

Fig. 3 Electron diffraction patterns of the: a) F-phase along the [110] zone axis and b) I-phase along the 5-fold direction.

Isothermal sections

The partial isothermal section at 1100 °C is presented in Fig. 4. In the studied compositional range the Al_2Ru and $Al_{13}Ru_4$ are solid at this temperature while the region adjacent to Al–Pd is occupied by the liquid. The limit of Al solubility in the β-phase (not shown in Fig. 4) reaches 56 at.% at 3.5 at.% Pd.

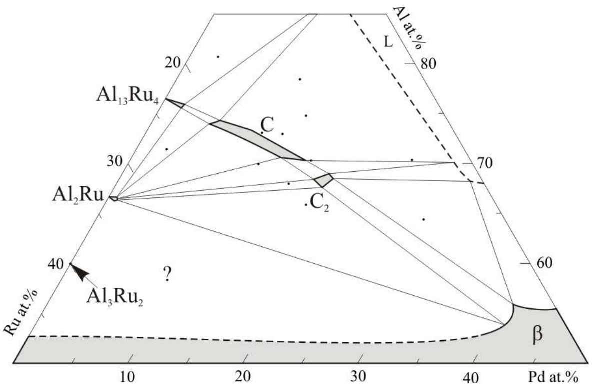

Fig. 4 Partial isothermal section of Al–Pd–Ru at 1100°C. The compositions of the studied alloys are marked by spots, the provisional tie-lines are shown by dotted lines, suggested regions of homogeneity of the phases by broken lines. The liquid is designated L, M-$Al_{13}Ru_4$ is M.

The $Al_{13}Ru_4$ and Al_2Ru phases extend up to ~2 and ~1 at.% Pd correspondingly. The ternary C-phase is formed in a wide range from ~$Al_{73.0}Pd_{5.0}Ru_{22.0}$ to $Al_{70.5}Pd_{15.0}Ru_{14.5}$. The C_2-phase is also solid at this temperature and occupies a small range around $Al_{68.5}Pd_{18}Ru_{13.5}$. It is in equilibrium with the liquid, C, Al_2Ru and the β-phase.

The phase equilibria at 1000 °C are shown in Fig. 5. The limit of Pd solubility in the M–$Al_{13}Ru_4$ phase increases to ~2.5 at.%, while that of Al_2Ru decreases to ~0.5 at.%. Apart from C and C_2 also I, F and ε are solid at this temperature. The regions of ternary phases are very close to each other, thus several ranges of the three-phase equilibria are

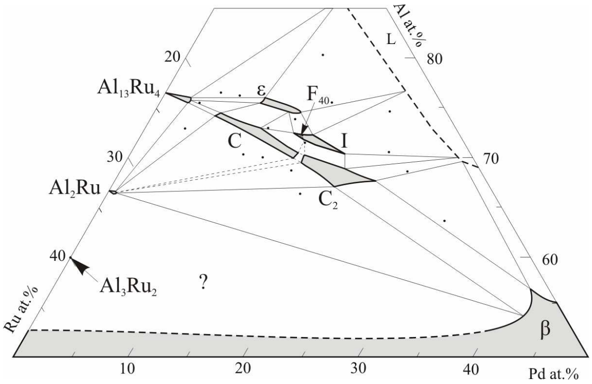

Fig. 5 Partial isothermal section of Al–Pd–Ru at 1000°C. The compositions of the studied alloys are marked by spots, the provisional tie-lines are shown by dotted lines, suggested regions of homogeneity of the phases by broken lines. The liquid is designated L, M-$Al_{13}Ru_4$ is M.

narrow. The corresponding tie-lines are shown approximately, on the basis of the results obtained from two-phase samples. The region of C_2 is significantly wider than at 1100°C namely from ~$Al_{70.5}Pd_{15.0}Ru_{14.5}$ to $Al_{68}Pd_{23}Ru_9$. The composition of the C-phase varies in the range from $Al_{74.5}Pd_5Ru_{20.5}$ to $Al_{72}Pd_{10}Ru_{18}$. The I-phase is formed in the compositional range between ~$Al_{72.5}Pd_{13.5}Ru_{14.0}$ and $Al_{70.0}Pd_{19.5}Ru_{10.5}$. The F-phase exists around the high-Ru limit of the I-region. The ε-range extends from ~$Al_{76.0}Pd_{8.5}Ru_{15.5}$ to $Al_{75}Pd_{12}$ Ru_{13}.

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