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Isothermal Section of the Al-Pd-Co Phase Diagram at 850 °C Delimited by Homogeneity Ranges of Phases Epsilon, U, and F

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Eight alloys with metal compositions (at.%) ranging between (68-76)Al, (9-25)Pd and (5-20)Co were investigated after annealing at 850 °C for 500 h. In the investigation, the scanning electron microscopy including energy dispersive x-ray spectroscopy and the x-ray diffraction were used. In the investigated alloys, various combinations of phases β, U, F, ε_6, ε_{16}, ε_{28}, δ, Al_5Co_2, and Al_9Co_2 were identified. Partial isothermal section at 850 °C of the Al-Pd-Co phase diagram was proposed, containing homogeneity ranges of six phases (ε_n, U, F, β, δ, and Al_5Co_2).

Keywords aluminum alloys, intermetallics, scanning electron microscopy, ternary phase diagram, x-ray diffraction

1. Introduction

Experimental studies of the Al-Pd-Co system comprising complex metallic alloys (CMA) were done by Yurechko et al.[1,2] and Cernickova et. al.[3] As a result, the authors proposed partial isothermal sections of the Al-Pd-Co phase diagram at 790, 940, 1000, 1050,[1,2] and 700 °C.[3] CMAs are mostly binary, ternary or quaternary systems containing mainly phases with giant unit cells and quasicrystals.[4-6] Many CMAs are not sufficiently known yet, inclusive of those related to the Al-Pd-Co system. Crystallographic parameters of binary and ternary phases reported for this system are summarized in Table 1.[1-3]

In this work, several phases of the ε-family (denoted jointly as ε_n),[7-9] F, and U were studied in more detail. Phases of the ε-family are classified as orthorhombic approximants of the decagonal quasicrystal.[1,2] In the Al-Pd-Co system, ε_6 and ε_{28} were classified as binary phases alloyed with the third element, and ε_{16}, ε_{22} and ε_{34} as ternary phases.[7] Structures of all of them consist of two different clusters, i.e. PMI (pseudo-Mackay icosahedra) and/or LBPP (large bicapped pentagonal prism).[8] Central points of the PMI clusters correspond to vertices of phason tiles of three different shapes (hexagon, pentagon, and banana-shape nonagon) if projected into a plane oriented perpendicularly to the phason plane. Recently, three types of tiling were reported, consisting of only hexagons (ε_6), pentagons and banana-shape nonagons (ε_{16}), and hexagons, pentagons and banana-shape nonagons (ε_{22}, ε_{28} and ε_{34}).[7-9] Ternary monoclinic U-phase with lattice parameters a = 1.9024 nm, b = 2.9000 nm, c = 1.3140 nm, and β = 117.26° was identified by Yurechko et al.[10] The metal composition of this phase was reported between $Al_{69.1}Pd_{18.5}Pd_{12.4}$ and $Al_{70.2}Pd_{11.4}Co_{18.4}$. In alloys $Al_{68}Pd_{14.6}Co_{17.4}$ and $Al_{69.8}Pd_{13.8}Co_{16.4}$, several isostructural mutations of the U-phase differing from each other in metal compositions were observed, also after long-term isothermal annealing.[11] It was shown that each of the mutations originated from other parent phase. The structure of cubic F-phase with lattice parameter 2.4397 nm was derived by Sugiyama et al.[12] This phase was experimentally observed by Yurechko et al.[10,13] in the triangular composition range between $Al_{71.2}Pd_{11.6}Co_{17.2}$, $Al_{71.4}Pd_{12.3}Co_{16.3}$, and $Al_{71.9}Pd_{11.5}Co_{16.6}$. In the long-term annealed $Al_{72}Pd_9Co_{19}$ alloy, two isostructural mutations of the F-phase were identified with very similar metal compositions.[14]

According to the findings of Yurechko et al.,[1] phases ε_n, F, and U could form single-phase areas in the temperature range 940-790 °C in the Al-Pd-Co phase diagram. However, changes of these areas with temperature were not proved experimentally till now. In the present work, therefore, the alloys $Al_{68}Pd_{14.6}Co_{17.4}$, $Al_{70}Pd_{25}Co_5$, $Al_{71.2}Pd_{15}Co_{13.8}$, $Al_{71}Pd_9Co_{20}$, $Al_{72.5}Pd_{21}Co_{6.5}$, $Al_{72.8}Pd_{15.6}Co_{11.6}$, $Al_{73.3}Pd_{12.8}Co_{13.9}$, and $Al_{76}Pd_{11}Co_{13}$ were long-term annealed at 850 °C and subsequently characterized. The experiments were done with the intention to propose a partial isothermal section of the Al-Pd-Co phase diagram at 850 °C, still missing in the literature. The attention was focused on the area delimited by homogeneity ranges of phases ε_n, U, and F.

2. Experimental Procedures

The investigated alloys were prepared by arc melting of pure components (Al, Pd, and Co) under argon atmosphere.

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Table 1 **Crystallographic data of phases in Al-Pd-Co system and corresponding binaries**[1-3]

		Lattice parameters			
Phase	**Space group or symmetry**	**a, nm**	**b, nm**	**c, nm**	**β, °**
Al-Co system					
Al_9Co_2	$P2_1/a$	0.85565	0.6290	0.62130	94.76
O-$Al_{13}Co_4$	$Pmn2_1$ or Pnmn	0.8158	1.2347	1.4452	…
M-$Al_{13}Co_4$	C2/m	1.5173	0.81090	1.2349	107.84
Z	monoclinic	3.984	0.8148	3.223	107.97
Al_5Co_2	$P6_3/mmc$	0.76717	…	0.76052	…
AlCo (β)	$Pm\bar{3}m$	0.2854	…	…	…
Al-Pd system					
ε_6	$Pna2_1$	2.35	1.68	1.23	…
ε_{28}	C2mm	2.35	1.68	5.70	…
Al_3Pd_2 (δ)	$P\bar{3}m1$	0.4227	…	0.5167	…
AlPd (β)	$Pm\bar{3}m$	0.3036	…	…	…
Al-Pd-Co system					
W	$Pmn2_1$	2.36	0.82	2.07	…
V	P121, P1m1 or P12/m1	1.0068	0.3755	0.6512	102.38
U	C121, C1m1 or C12/m1	1.9024	2.9000	1.3140	117.26
F	$P2_1/a\bar{3}$	2.4397	…	…	…
C_2	$Fm\bar{3}$	1.5507	…	…	…
Y_2	Immm	1.5451	1.2105	0.7590	…
ε_{16}	Orthorhombic	2.35	1.68	3.26	…
ε_{22}	Orthorhombic	2.35	1.68	5.70	…
ε_{34}	Orthorhombic	2.35	1.68	7.01	…

After casting, the samples were annealed at 850 °C for 500 h and rapidly cooled in water to preserve their high-temperature microstructures. In the investigation, the scanning electron microscopy (SEM) including energy dispersive x-ray spectroscopy (EDX), and the x-ray diffraction (XRD) were used.

Particular microstructure constituents were observed and their metal compositions were determined by a JEOL JSM-7600F scanning electron microscope operating at the acceleration voltage of 20 kV in regimes of secondary electrons (SEI) or back-scattered electrons (BEI). The microscope was equipped with an Oxford Instruments X-max50 spectrometer for EDX analysis including INCA software. At least 10 measurements per constituent were done to obtain mean values of metal compositions. Volume fractions of the constituents were determined by means of the ImageJ software.

An x-ray Panalytical Empyrean PIXCel 3D diffractometer with Bragg-Brentano geometry was used for the phase identification. The characteristic $CoK\alpha_{1,2}$ radiation was generated at 40 kV and 40 mA. Measurements were done in the angular range 10° to 140°, with the step size of 0.0131°, and the counting time 98 s/step.

3. Results

Microstructures of all the investigated alloys are documented in Fig. 1. They are formed with single-phase constituents only; to each constituent the respective phase identified by XRD is assigned. XRD patterns corresponding to particular alloys are shown in Fig. 2. Metal compositions and volume fractions of the microstructure constituents coupled with the identified phases are given in Table 2.

In the $Al_{68}Pd_{14.6}Co_{17.4}$ alloy, three microstructure constituents were observed (Fig. 1a). Two of them were identified as phases U and β (Fig 2a), the third constituent showed metal composition close to binary Al_5Co_2 with the maximum solubility of Pd about 2.9 at.% (Table 2). In the $Al_{70}Pd_{25}Co_5$ alloy, two microstructure constituents were observed (Fig. 1b) corresponding to phases δ and ε_n (ε_n is the mixture of ε_6 and ε_{28}), Fig. 2(b). The maximum solubility of Co in binary δ (Al_3Pd_2) was determined as about 0.9 at.% (Table 2). The microstructure of the $Al_{71.2}Pd_{15}Co_{13.8}$ alloy consists of two constituents identified as U and ε_n ($\varepsilon_6 + \varepsilon_{28}$), Fig. 1(c) and 2(c). In the microstructure of the $Al_{71}Pd_9Co_{20}$ alloy, two constituents were found, identified as F and Al_5Co_2 (Fig. 1d, 2d). The maximum solubility of Pd in binary Al_5Co_2 was determined to be 3.0 at.% (Table 2). Single-phase microstructures of alloys $Al_{72.5}Pd_{21}Co_{6.5}$, $Al_{72.8}Pd_{15.6}Co_{11.6}$, and $Al_{73.3}Pd_{12.8}Co_{13.9}$ are formed with ε_n (Fig. 1e-g, 2e-g). The mixture of two binary phases $\varepsilon_6 + \varepsilon_{28}$ was identified in alloys $Al_{73}Pd_{20}Co_7$ and $Al_{73.5}Pd_{15}Co_{11.5}$ (Fig. 2e, f). The ternary ε_{16} phase was found in the $Al_{73.8}Pd_{12.8}Co_{13.4}$ alloy (Fig. 2g). The double-phase microstructure of the $Al_{76}Pd_{11}Co_{13}$ alloy contains ternary (ε_{16}) and binary (Al_9Co_2) phases, Fig. 1(h) and 2(h).

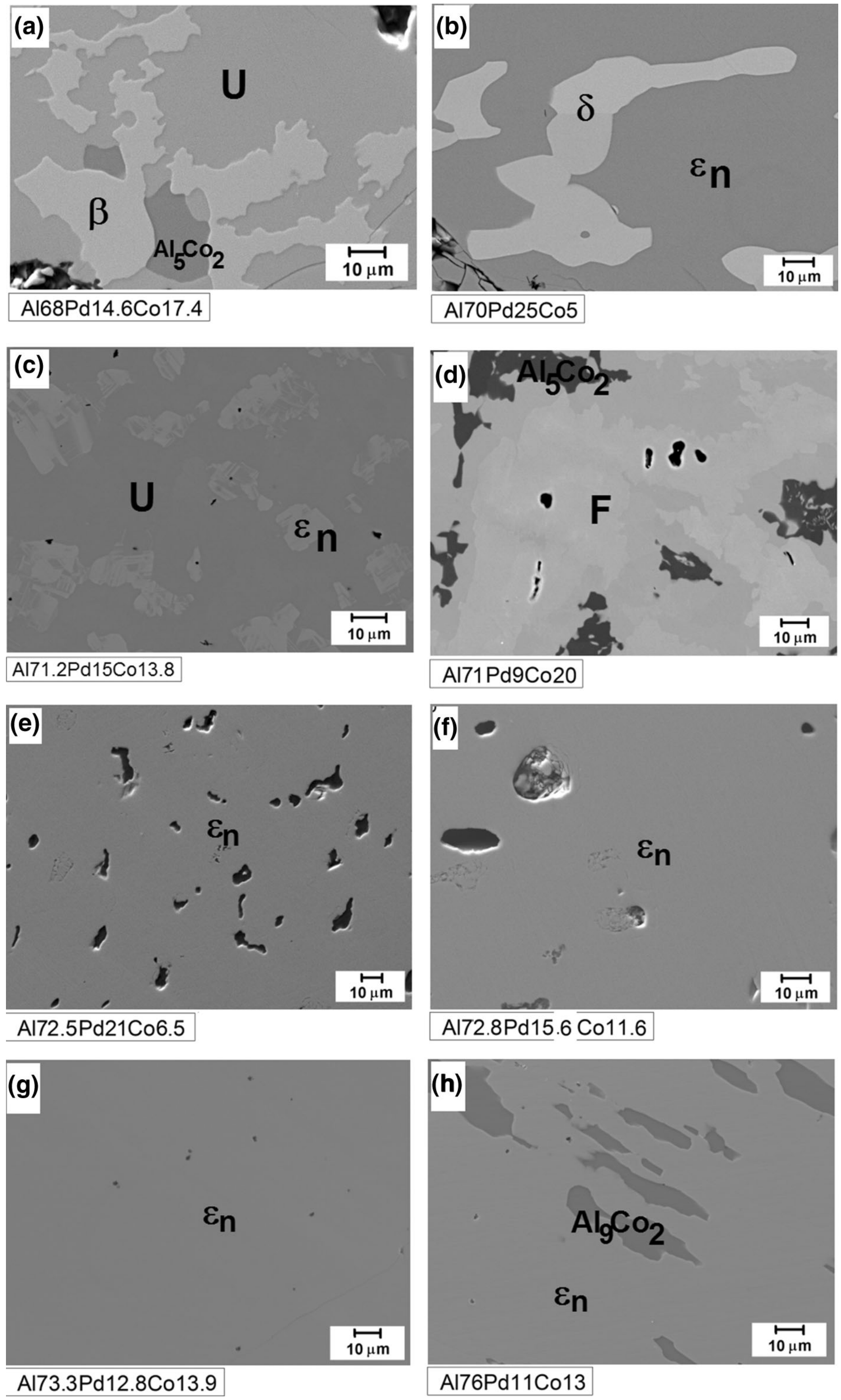

Fig. 1 Microstructures of investigated alloys. To each microstructure constituent corresponding phase is assigned. Documented by BEI/SEM

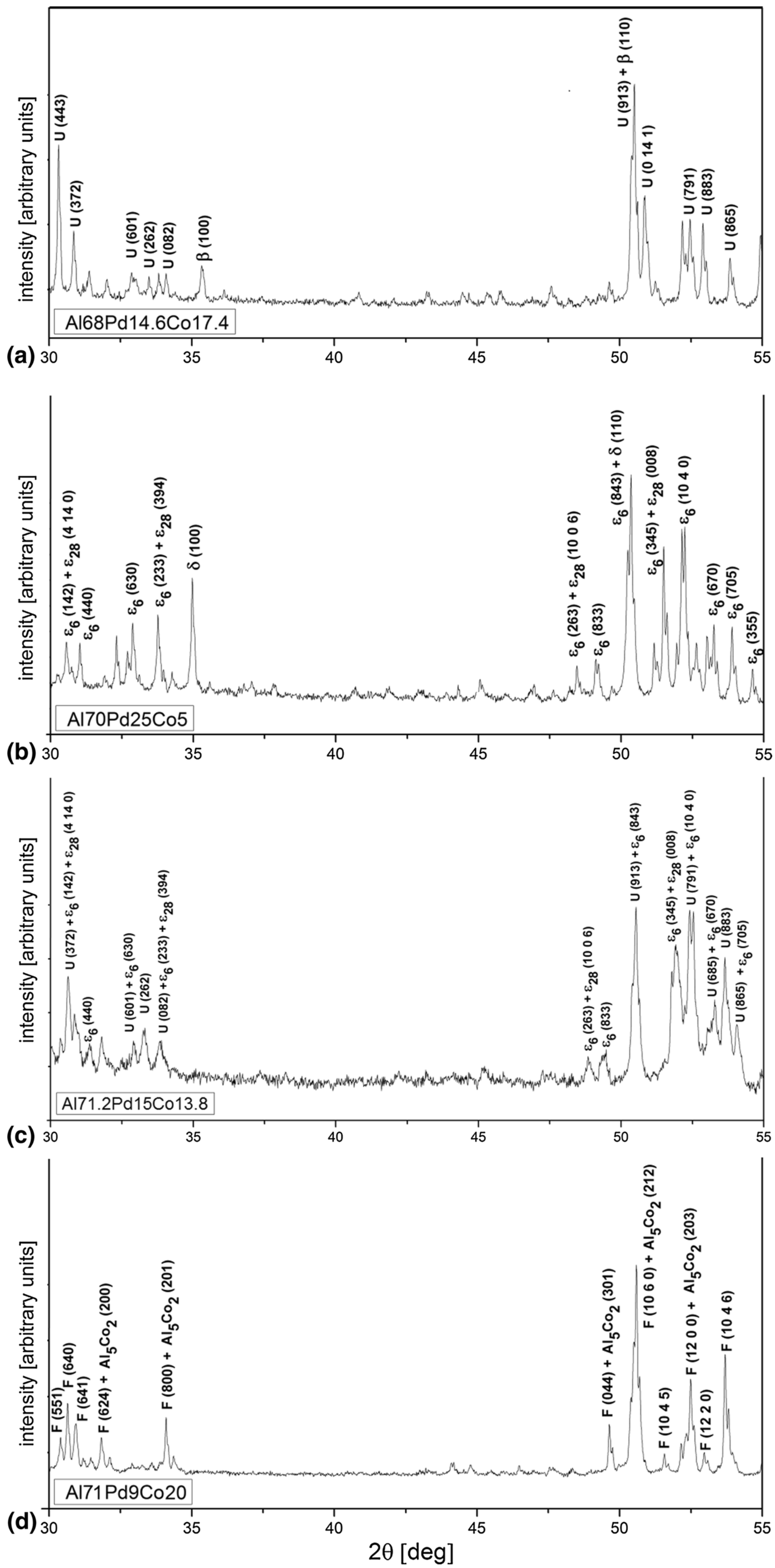

Fig. 2 Powder x-ray diffraction patterns corresponding to investigated alloys

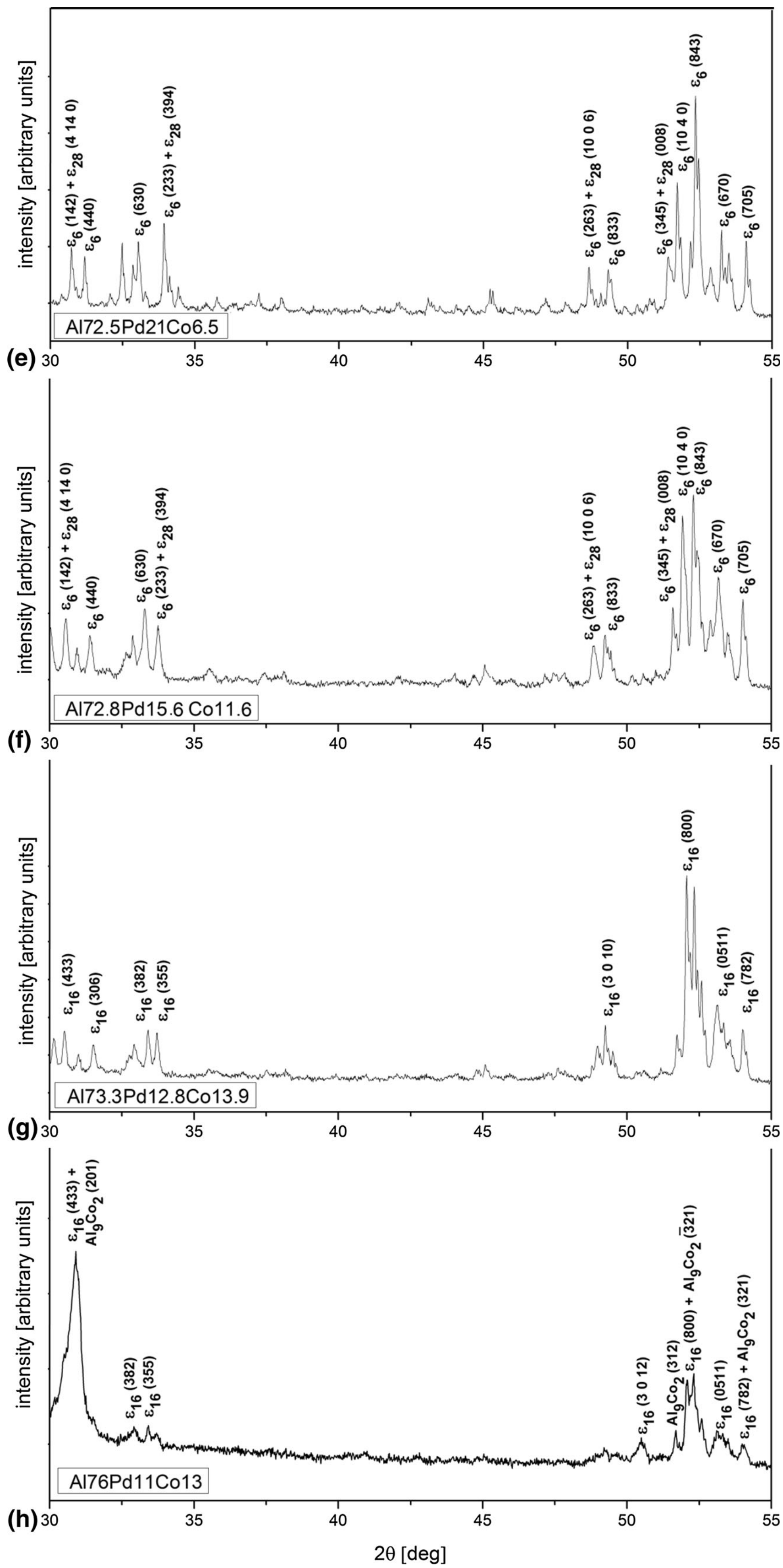

Fig. 2 continued

Table 2 Metal compositions and volume fractions of observed microstructure constituents

Alloy	Microstructure constituent	Phase	Atomic content in %: Al	Pd	Co	Volume fraction in %
$Al_{68}Pd_{14.6}Co_{17.4}$	White	β	55.5 ± 0.1	24.8 ± 0.2	19.7 ± 0.2	21
	Dark-grey	U	69.1 ± 0.2	14.4 ± 0.3	16.5 ± 0.3	75
	Dark	Al_5Co_2	71.1 ± 0.3	2.9 ± 0.3	26.0 ± 0.4	4
$Al_{70}Pd_{25}Co_5$	White	δ	58.8 ± 0.4	40.3 ± 0.2	0.9 ± 0.2	22
	Grey	ε_n (ε_6+ε_{28})	73.1 ± 0.2	20.9 ± 0.2	6.0 ± 0.3	78
$Al_{71.2}Pd_{15}Co_{13.8}$	Grey	ε_n (ε_6+ε_{28})	72.7 ± 0.3	12.7 ± 0.2	14.6 ± 0.1	42
	Dark-grey	U	69.8 ± 0.2	15.8 ± 0.1	14.4 ± 0.3	58
$Al_{71}Pd_9Co_{20}$	Grey	F	70.5 ± 0.4	11.8 ± 0.2	17.7 ± 0.2	71
	Dark	Al_5Co_2	71.5 ± 0.2	3.0 ± 0.4	25.5 ± 0.3	29
$Al_{72.5}Pd_{21}Co_{6.5}$	Grey	ε_n (ε_6+ε_{28})	72.5 ± 0.3	21.0 ± 0.2	6.5 ± 0.4	100
$Al_{72.8}Pd_{15.6}Co_{11.6}$	Grey	ε_n (ε_6+ε_{28})	72.8 ± 0.2	15.6 ± 0.2	11.6 ± 0.1	100
$Al_{73.3}Pd_{12.8}Co_{13.9}$	Grey	ε_n (ε_{16})	73.3 ± 0.1	12.8 ± 0.3	13.9 ± 0.2	100
$Al_{76}Pd_{11}Co_{13}$	Grey	ε_n (ε_{16})	74.8 ± 0.1	14.0 ± 0.2	11.2 ± 0.1	78
	Dark	Al_9Co_2	82.4 ± 0.4	1.8 ± 0.4	15.8 ± 0.3	22

Experimentally determined bulk metal compositions of investigated alloys are given in the first column; phases corresponding to particular constituents are given the third column

The maximum solubility of Pd in the latter phase was determined as about 1.8 at.% (Table 2).

4. Discussion

In the investigated alloys, various combinations of phases β, U, F, ε_6, ε_{16}, ε_{28}, δ, Al_5Co_2, and Al_9Co_2 were identified after long-term annealing at 850 °C (Fig. 1, 2; Table 2). The phases classified under the ε-family (ε_6, ε_{16}, and ε_{28}) were found in six of eight investigated alloys. For the alloys with a lower bulk Al content and the dominance of Pd over Co, the doublet $\varepsilon_6 + \varepsilon_{28}$ is characteristic. On the other hand, the single ε_{16} phase was found in alloys showing a higher Al content and the dominance of Co over Pd (Fig. 2; Table 2). The U-phase was present in alloys $Al_{68}Pd_{14.6}Co_{17.4}$ and $Al_{71.2}Pd_{15}Co_{13.8}$ with the bulk ratios Al:Pd:Co equal to about 70:15:15. The F-phase was identified in the $Al_{71}Pd_9Co_{20}$ alloy with the highest bulk Co content, Table 2. Thus, cobalt was considered to stabilize this phase. Similarly, the presence of δ in the $Al_{70}Pd_{25}Co_5$ alloy containing the highest amount of Pd (Table 2) shows δ has to be stabilised by Pd.

Experimentally determined partial isothermal section of the Al-Pd-Co phase diagram at 850 °C is illustrated in Fig. 3. In the isothermal section, homogeneity ranges of six phases (ε_n, U, F, β, δ, and Al_5Co_2) are sketched. According to positions of the homogeneity ranges, F, U, and ε_n can be characterized as ternary phases at 850 °C. As follows from the earlier results of Yurechko et al.,[1] F and U are ternary phases in a wider temperature range, at least between 790 and 940 °C. The expectation following from the comparison of isothermal sections at 790 and 940 °C about the shrinkage of F and U homogeneity ranges with decreasing

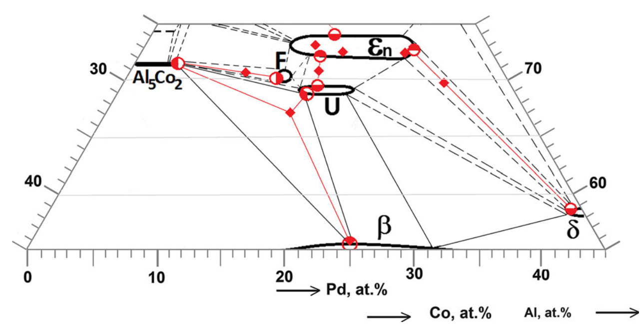

Fig. 3 Experimentally determined partial isothermal section of Al-Pd-Co phase diagram at 850 °C. Squares represent positions of investigated alloys, half-solid circles positions of phases in double-phase alloys, and third-solid circles positions of phases in triple-phase alloy. Bold solid lines characterize positions of phase homogeneity ranges. Fine solid and dashed lines are precise and estimative boundaries between multi-phase areas, respectively. Triple- and double-solid circles corresponding to the Al_5Co_2 area are overlapped, thus the former circle is not observable

temperature[1] was also confirmed in the present work; more evidently for the F-phase. On the other hand, ε_n classified as a binary family of phases at temperatures below 790 °C[1,15] should expand into triple-phase space at temperatures above 790 °C that was also confirmed in the present work for phases ε_6, ε_{16}, and ε_{28}. Moreover, ε_6 and ε_{28} containing up to 14.6 at.% Co (Table 2) considered earlier as binary Al-Pd phases (Table 1) were now identified at 850 °C in Al-Pd-Co alloys. Based on this finding, a strict distinguishing between binary (ε_6 and ε_{28}) and ternary (e.g. ε_{16}) phases inside the ε-family seems to be questionable. As follows from the comparison of the isothermal section at 850 °C, Fig. 3, and isothermal sections at 790 and 940 °C,[1] the homogeneity range of ε_n shrinks with increasing temperature. The results obtained in this work confirmed that β, δ, and Al_5Co_2 are binary phases alloyed with the third element (compare Tables 1, 2).

5. Conclusions

Eight alloys with metal compositions (at.%) ranging between (68-76)Al, (9-25)Pd and (5-20)Co were investigated after annealing at 850 °C for 500 h. The results obtained can be summarized as follows:

(1) Various combinations of phases β, U, F, ε_6, ε_{16}, ε_{28}, δ, Al_5Co_2, and Al_9Co_2 were identified in the investigated alloys.
(2) Phases ε_6 and ε_{28} containing up to 14.6 at.% Co were identified at 850 °C in alloys $Al_{70}Pd_{25}Co_5$, $Al_{71.2}Pd_{15}Co_{13.8}$, $Al_{72.5}Pd_{21}Co_{6.5}$, and $Al_{72.8}Pd_{15.6}Co_{11.6}$. Earlier they were considered as binary phases stable below 790 °C in the Al-Pd system.
(3) The single ε_{16} phase was found in alloys $Al_{73.3}Pd_{12.8}Co_{13.9}$ and $Al_{76}Pd_{11}Co_{13}$, showing higher Al contents and the dominance of Co over Pd.
(4) The U-phase was found in alloys $Al_{68}Pd_{14.6}Co_{17.4}$ and $Al_{71.2}Pd_{15}Co_{13.8}$ with the approximate bulk ratios Al:Pd:Co=70:15:15.
(5) The F-phase was identified in the $Al_{71}Pd_9Co_{20}$ alloy, having the highest bulk Co content of the investigated alloys.
(6) Partial isothermal section at 850 °C of the Al-Pd-Co phase diagram was proposed, containing homogeneity ranges of six phases (ε_n, U, F, β, δ, and Al_5Co_2).

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