CONTRIBUTION TO ASSESSMENT OF TERNARY Al-Pd BASED SYSTEMS

ŠTÚDIUM TERNÁRNYCH SYSTÉMOV NA BÁZE Al-Pd

Martin KRIŠKA, Ľubica KAHALOVÁ, Martin KUSÝ, Jozef JANOVEC

Institute of Materials, Faculty of Materials Science and Technology, Slovak University of Technology, Bottova 23, 917 24 Trnava, Slovak Republic,
martin.kriska@stuba.sk

Abstract:

The characterization of phases in ternary complex metallic alloys (72.8Al-11.6Pd-15.6Rh annealed at 1100˚C for 49 h, and 73.5Al-11Pd-15.5Co annealed 1000˚C for 92 h) was performed. In the investigation, light microscopy, differential thermal analysis, and scanning electron microscopy including energy and wavelength dispersive X-ray spectroscopy were used. The dominant constituent in the original state of the 72.8Al-11.6Pd-15.6Rh alloy was characterized as ε – phase. The minor constituent was attributed to the additionally solidified liquid co-existing with ε – phase at 1100˚C. After differential thermal analysis, the microstructure was composed of the matrix ε – phase and areas of the creek-type morphology. For the 73.5Al-11Pd-15.5Co alloy, original state as well as the state after thermal cycling were found to consist of the same microstructure constituents corresponding to the ternary U-phase, binary δ – phase, and non-identified phase. The U – phase showed the compositional stability in a broad temperature range. The stability of the δ – phase during cooling was found to be accompanied with the decrease of cobalt content.

Abstrakt:

V rámci štúdia ternárnych komplexných kovových zliatin (72.8Al-11.6Pd-15.6Rh žíhaná pri 1100 ˚C počas 49 h, a 73.5Al-11Pd-15.5Co žíhaná pri 1000 ˚C počas 92 h) bola vykonaná charakterizácia prítomných fáz. Zliatiny boli skúmané pomocou svetelnej mikroskopie, diferenčnej termálnej analýzy ako aj rastrovacej elektrónovej mikroskopie zahrňujúcej energiovo a vlnovo disperznú analýzu. Majoritná zložka vo východiskovom stave zliatiny 72.8Al-11.6Pd-15.6Rh bola identifikovaná ako ε – fáza. Minoritná zložka bola priradená dodatočne stuhnutej tavenine koexistujúcej s ε - fázou pri 1000˚C. Po diferenčnej termálnej analýze došlo v mikroštruktúre zliatiny k zmene morfológie.

V prípade štúdia zliatiny 73.5Al-11Pd-15.5Co vo východiskovom stave ako aj stave po diferenčnej termálnej analýze bola preukázaná prítomnosť ternárnej U - fázy, binárnej δ – fázy a neidentifikovanej fázy. Pri U – fáze bola preukázaná jej stabilita v širokom teplotnom rozsahu. Taktiež bola preukázaná stabilita δ – fázy sprevádzaná s poklesom obsahu kobaltu.

Keywords: Complex metallic alloys, Al–Pd–Rh, Al-Pd-Co, Scanning electron microscopy, Differential thermal analysis

Kľúčové slová: Komplexné kovové zliatiny, Al-Pd-Rh, Al-Pd-Co, Rastrovacia elektrónová mikroskopia, Diferenčná termálna analýza

1 INTRODUCTION

In the last decades, special alloy based on binary, ternary, or quaternary systems, referred to as complex metallic alloys (CMA), have been studied in addition to the “normal“materials of the mass production. In general, a very small group of these CMAs has been investigated and developed for use from a huge variety of possible metallic systems [1]. In these multicomponent alloys, phases form crystal structures based on giant unit cells where the atoms arranged in clusters of icosahedral coordination play a prominent role. As a consequence, the structures of CMAs show often duality; they are periodic crystals on the scale of several nanometers, whereas they resemble quasicrystals on the atomic scale. In accordance with mentioned, most physical properties of CMAs show distinct differences with respect to the behavior of “normal” metallic alloys and therefore they are of interest for potential technological applications [2-7].

Among the CMAs, the binary Al-Tm systems (Tm = transition metal) containing 60 – 85 at. % of aluminum and the ternary Al-Tm-Tm systems have been investigated mostly. These extensive studies have demonstrated a need for reconsideration of binaries and ternaries of the concerned systems. In the recent studies of Al-Pd-Fe, Al-Pd-Co, and Al-Pd-Rh systems, the concentration ranges of ε–, C–,V–, and other phases were determined at different temperatures [8-10].

The intention of the authors of this paper is to characterize phases present in the 72.8Al-11.6Pd-15.6Rh, and 73.5Al-11Pd-15.5Co alloys and to compare the microstructures and the alloys. The influence of thermal cycles on stability and evolution of phases in the alloys was also considered.

2 EXPERIMENTAL

Bulk samples were prepared by melting the pure constituents under a helium atmosphere in an induction furnace. The as-cast ingots were then crushed into powder of granulometric fraction between 20 and 50 μm. The powder was compacted in a graphite cell and sintered at high temperature using a uniaxial pressure of 15 MPa. The samples were subsequently annealed at conditions given in Table 1. The microstructure and properties of the sintered and annealed bulk materials were studied with light microscopy (LM), scanning electron microscopy (SEM) include energy dispersive X-ray spectroscopy (EDX) and wavelength dispersive X-ray spectroscopy (WDX), and high-temperature differential thermal analysis (DTA).

Table 1 Overview of annealing parameters

	Annealing temperature	Time of annealing
72.8Al-11.6Pd-15.6Rh	1100˚C	49 h
73.5Al-11Pd-15.5Co	1000˚C	92 h

3 RESULTS

3.1 ORIGINAL STATE

3.1.1 72.8Al-11.6Pd-15.6Rh alloy

The microstructure of the original state consists of two microstructural constituents. The dominant bright areas correspond to the matrix, while the minor dark sharp bounded areas are distributed in the matrix unevenly, Fig. 1 (a).

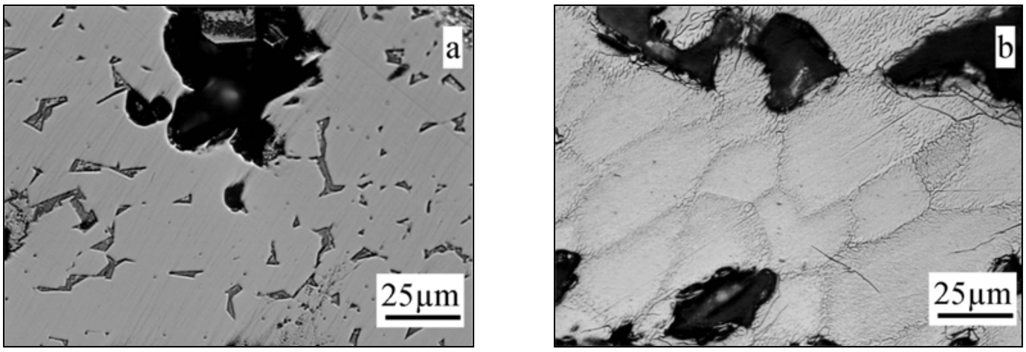

Figure 1 Microstructures of the original state (a) and the state after DTA (b). The samples were etched by Keller

In Fig. 2, distributions of aluminium (b), palladium (c), and rhodium (d) in particular phases present in the microstructure (a) are documented. The EDX mapping confirmed the inhomogeneous distribution of analyzed elements. The enhanced content of palladium and the reduced amount of rhodium were found in the dark constituent in comparison to the matrix. This finding was also confirmed by the line EDX analysis (see ref. [8]).

Additionally to the EDX, chemical compositions of the particular microstructural constituents were determined by WDX (Table 2).

Table 2 Average values of chemical composition of particular microstructural constituents measured by wavelength dispersive X-ray spectroscopy

	Chemical composition [at %]		
	Al	Pd	Rh
Matrix – bright area	72.3±0,7	9.2±0.6	18.5±0.3
Dark area	74.2±1.8	21.8±2.3	4±1.6
Areas in pores	84±2.1	13±0.4	3±0.3

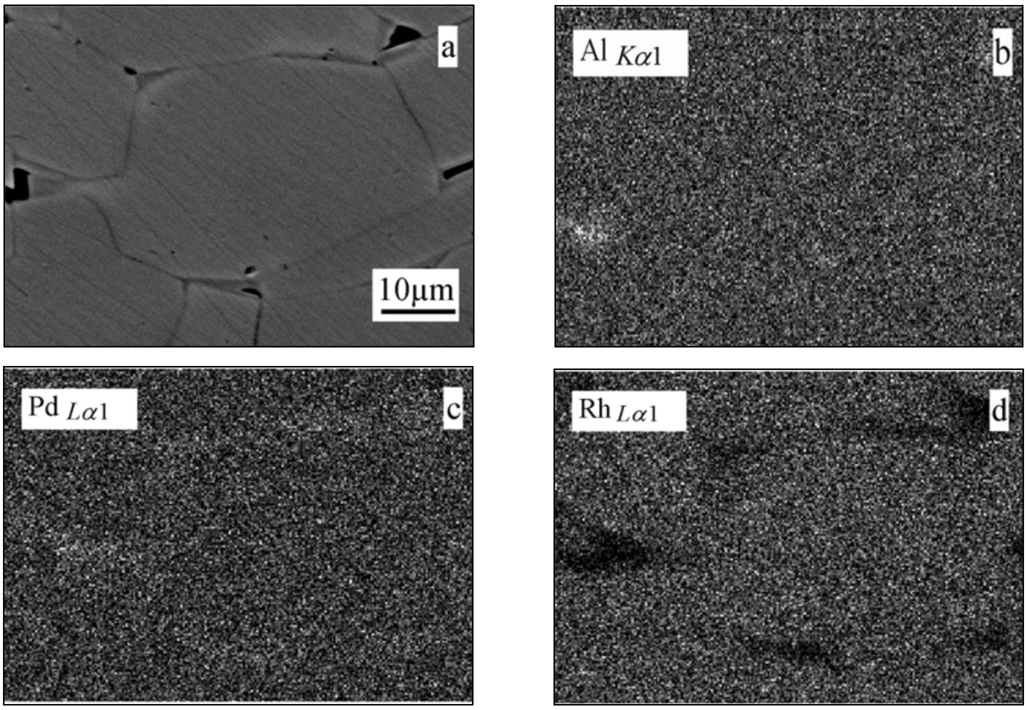

Figure 2 Back-scattered electron micrograph of the analysed area in the original state (a). The maps of aluminium (b), palladium (c) and rhodium (d) distributions

3.1.2 73.5Al-11Pd-15.5Co alloy

Light micrograph of the alloy in original state is shown in Fig. 3a. It consist of more areas exhibiting different colors. The charcoal areas (marked with 2) dominating in the microstructure form discrete grains of various sizes and shapes. The white mainly longitudinal areas (marked with 3) are randomly distributed in the whole volume. The grey areas (marked with 1) form continuous network around the discrete charcoal and white grains.

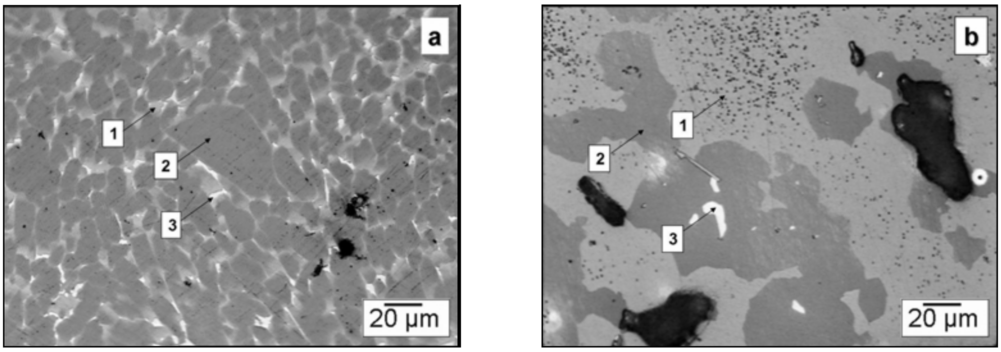

Figure 3 Light micrographs of (a) as-received state, (b) state after DTA. The grey, charcoal, and white areas are marked by symbols 1, 2, and 3, respectively

For gaining the exact chemical composition of the observed areas, EDX as well as WDX analyses were used. The average concentrations from WDX are listed in Table 3. Literature data concerning the chemical compositions of the phases identified in the Al-Pd-Co system are also given in Table 3. By comparison of the measured values with the literature data the phases supposed to be present in the studied alloy were determined.

Table 3 Measured chemical compositions of observed areas by wavelength dispersive X-ray spectroscopy compared with literature data published for Al-Pd-Co system

Phase	Measured chemical composition at.%			Chemical composition according to [9] at.%			Supposed phase
	Al	Pd	Co	Al	Pd	Co	
Charcoal	70.51±0.04	15.15±0.15	14.34±0.11	69.1	16.5	14.4	U
	70.21±0.08	19.46±0.73	10.34±0.81				
White	59.52±1.27	39.05±0.98	1.43±0.28	≤ 61.1	≥ 34.9	up to 4	Al_3Pd_2 (δ)
	56.48±0.11	42.32±0.14	1.22±0.04				
Grey	69.84±0.41	20.76±4.43	9.40±4.02				
	68.44±1.43	23.90±0.85	7.68±0.58				

3.2 STATE AFTER DTA

3.2.1 72.8Al-11.6Pd-15.6Rh alloy

In Figs. 4-5, a representative and reproducible enough behaviour of studied material during differential thermal analysis is documented (shapes of the curves corresponding to the first and second runs are similar). The DTA measurements confirmed presence of two phases in the studied system.

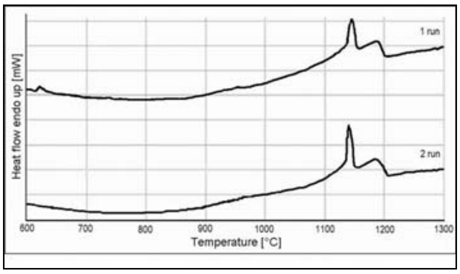

Figure 4 Detailed view of the DTA heating curves +10°C /min

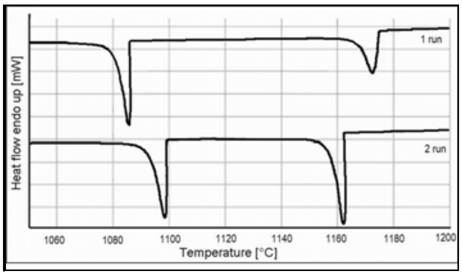

Figure 5 Detailed view of the DTA cooling curves at –10°C /min

In Fig. 4, a detail look is illustrated on heating curves containing peaks at temperatures 1145 and 1189°C in the first, and 1141 and 1186°C in the second runs. It indicates melting of probably two phases of the original state during heating. Accordingly, two solidifying peaks (corresponding to the same phases) at temperatures 1173 and 1086°C in the first, and 1162 and 1099°C in the second runs were observed, Fig. 5. The total energies of melting were determined to be equal to 225 and 234 J/g for the first and the second runs of heating, respectively. Similarly, the total energy of solidifying is equal to -237 J/g (the first run) and -211 J/g (the second run).

In comparison to the original state, the microstructure of the samples after DTA was changed (see Figs. 1a and 1b). In the latter microstructure the bright areas are separated by darker transition strips exhibiting „creek“morphology after etching for longer times (Fig.1b).

3.2.2 73.5Al-11Pd-15.5Co alloy

The microstructure of the alloy after the DTA, Fig. 3b, contains identical areas as documented for the original state.

DTA of the original state was performed in the temperature range from 20 to 1334°C. The experiment consisted of two heating and two cooling runs as it is shown in Fig. 6a, b. The heating curves exhibit three slightly overlapped peaks for each run, whereas the cooling curves contain two peaks with sharp onsets and in the second run a hint of the third peak. Small variations in reaction enthalpies for each cooling (ΔH = -305 J/g in the first run and -316 J/g in the second run, always ±2 J/g) and heating (ΔH = 323 J/g in the first run and 317 J/g in the second run) runs were observed. The enthalpy of the first melting is higher than that of the second melting. However it characterizes the original sample, a state slightly different from the DTA heat-treated one. Differences between the reaction enthalpies corresponding to the heating and cooling regimes of the same run do not exceed 12 J/g (approximately 4%).

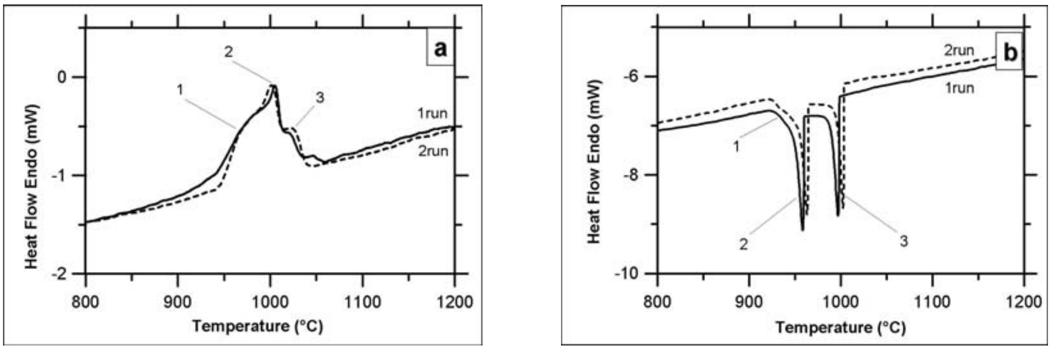

Figure 6 DTA record of analyzed sample: (a) heating curves, (b) cooling curves. Symbols 1, 2, and 3 were used to label peaks corresponding to grey, charcoal, and white areas, respectively

4 DISCUSSION

4.1 72.8Al-11.6Pd-15.6Rh ALLOY

It can be derived from the DTA curves that liquid phase exists in the alloy at temperatures above 1100°C (Fig. 5). On the other hand, solid phases should start to disappear slightly above 1100°C, Fig. 4. Thus, the occurrence of liquid in the alloy during annealing at 1100°C for 49 h cannot be excluded. To analyse the presence of phases in the alloy during the annealing, the isothermal section of the ternary Al-Pd-Rh diagram for 1100°C reported by Przepiorzynski et al. [10] was used (Fig. 7). It was shows that the bright area is formed with ε phase. It can be stated the sharp bounded dark-colour areas resembling intergranular triple points correspond to the remaining liquid phase solidified during the cooling from the annealing temperature.

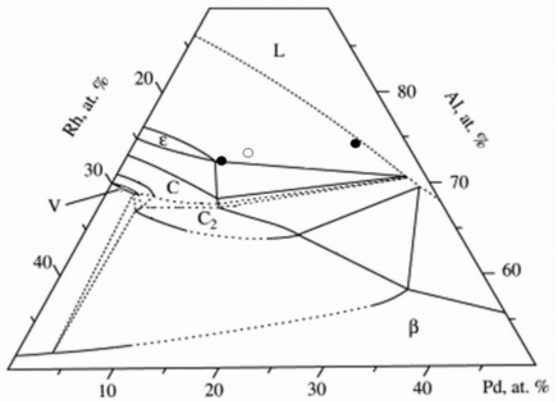

Figure 7 Isothermal section of the ternary Al-Pd-Rh diagram for 1100°C [10].The empty circle represents the average chemical composition of the investigated alloy. The solid circles correspond to chemical compositions of identified microstructure constituents

The total energies of solidification and melting are similar to one another regardless of the run order (1st or 2nd). With respect to the obtained results, the ε phase forms during cooling directly from the liquid. This reaction corresponds to the peaks at 1173 and 1162°C in the first and the second runs, respectively (Fig. 6). After the formation of ε phase is finished, the rest of liquid localised along the ε-areas starts to solidify at temperatures 1086 and 1099°C for the first and the second runs, respectively (Fig. 5). The lastly solidified areas in the state after DTA exhibit the creek-type microstructure (Fig. 1b). The occurrence of the creeks can be associated with some kind of heterogeneity. The rest liquid co-existing with the ε-phase at 1100°C should transform into ε-phase during cooling. The formation of many nuclei during the cooling and the non-coordinated growth of them result in the heterogeneous microstructure formed by creeks.

4.2 73.5Al-11Pd-15.5Co ALLOY

The alloy consists at least of three areas differing from each other in color as it is shown in Fig. 3a. The position of the alloy in the ternary Al-Pd-Co system is illustrated in Fig. 8. The solid and empty circles represent nominal and real chemical compositions of the alloy, respectively. The dashed curves point out chemical compositions of constituents corresponding to grey (1), charcoal (2) and white (3) areas characterized by light microscopy and WDS (EDS) analysis. The major charcoal area was found to contain about 15 at.% of both palladium and cobalt next to aluminum (Tab. 3). It is situated close to the single U-phase region in the ternary diagram (Fig. 8). The minor white area is palladium-rich and contains traces of cobalt. In the ternary diagram it falls into the liquid+β region. The grey area forming network along the charcoal areas showed enhanced palladium and reduced cobalt contents related to the nominal alloy composition. This constituent corresponds to the elliptic object situated in the three-phase liquid+U+δ region of the ternary diagram at 1000°C. As follows from the results obtained by light microscopy (Fig. 3a) and DTA (Fig. 6), the charcoal area (marked also 2 in this work) corresponds to the U-phase and the white area (marked also 3) is the binary Al_3Pd_2 (δ-phase) alloyed with cobalt. The DTA curves indicate the presence of liquid phase in the alloy at temperatures about 1000°C. This is also in accordance with the isothermal section of ternary diagram for 1000°C presented by Yurechko et al. [9], Fig. 8.

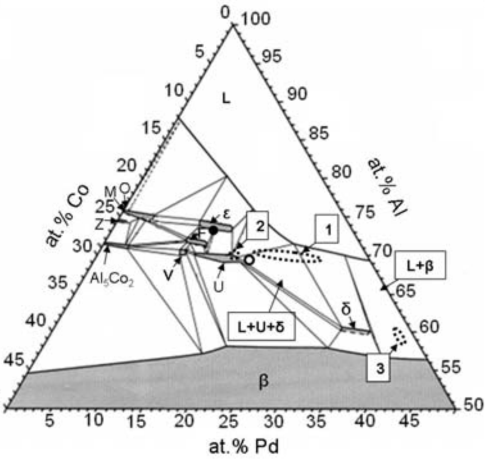

Figure 8 Partial isothermal section of Al-Pd-Co at 1000°C [9]

The sample after DTA consists of the same microstructural constituents (phases) showing the same colors (compare Figs. 3a and 3b) as the sample of the original state. Thus, the sample after DTA contains the U-phase (marked with symbol 2 in Figs. 3 and 8), the δ–phase (3) and solidified liquid (1) as it was identified for the original state. The volume portions of U- (2) and δ- (3) phases decreased and the volume portion of the solidified liquid increased after thermal cycling if compared to the original state (Fig. 3). It is acceptable, because the holding time at 1000°C of the DTA tested sample was about 6 seconds and the total cooling time took about 2 h. For comparison, the annealing time of the original sample was 92 h. It can be expected that the conditions at DTA did not allow the growth of the U- and δ-phases from liquid in near equilibrium amount. As a result, the volume portion of the gray constituent (47.3%) is significantly higher than it was determined for the original state (Table 3).

4.3 CONCLUDING REMARKS

The alloys investigated show similar chemical compositions. The contents of aluminium, palladium and the second transition metallic element are comparable, fulfilling the scheme 73-11-16. The only difference resides in the type of the second transition element (Rh versus Co). The replacement of Rh with Co resulted in more complicated ternary diagram at 1000-1100°C.

5 CONCLUSIONS

In the 72.8Al-11.6Pd-15.6Rh alloy annealed at 1100˚C for 49 h, two metallographically distinguishable areas have been observed. The dominant constituent was characterized as ε -phase. The minor constituent was attributed to the liquid (subsequently solidified) co-existing with ε - phase at 1100°C. After DTA, the microstructure of the alloy was composed of the matrix (ε - phase) and areas of the creek-type morphology.

In the 73.5Al-11Pd-15.5Co alloy annealed 1000˚C for 92 h, ternary U-phase, binary δ-phase and a non-identified phase were found. After the DTA, the volume portions of U- and δ-phases in the microstructure decreased opposite to the non-identified phase.

It was confirmed experimentally that the presence of cobalt (instead of rhodium) caused in the investigated Al-Pd-Tm alloys the formation of more ternary phases (e.g. V, U) and the shift of binary phases (e.g. δ, ε) into ternary areas. The formation enthalpies of Co-containing phases were found to be higher compared to Rh-containing phases.

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