

The Al–Co–Pd *R*-phase identity

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Abstract

The rhombohedral Al–Co–Pd *R*-phase ($\text{Al}_{73}\text{Co}_{13.5}\text{Pd}_{13.5}$, $R\bar{3}$, $a = 2.91019$ nm, $c = 1.31854$ nm) reported by R. Simura *et al.* (Metal. Trans. JIM 54 (2013) 1385) was identified with the Al–Co–Pd U-phase (*C*-centered, monoclinic), previously reported by M. Yurechko *et al.* (J. Alloys Comp. 337 (2002) 172). Following a crystallographic group-subgroup analysis, the relationship of the two structural descriptions was proposed, pointing to a possible rhombohedral pseudo-symmetry of the monoclinic U-phase or a monoclinic distortion in the rhombohedral structure.

Keywords: Crystal structure; Phase diagrams; Al–Co–Pd; Group-subgroup structural relationship.

Extensive investigation of the Al–Co–Pd constitutional diagram^[1] revealed a wide ternary extension of the Al–Pd ϵ -phase(s) region and the formation of six ternary phases, designated W, Y₂, U, V, F and C₂. The overall compositions of these phases, as determined there, are reproduced in Fig. 1.

In a more recent research by Simura *et al.*^[2], a new rhombohedral Al–Co–Pd phase, so-called *R*-phase, with the unit cell parameters mentioned in Table 1 (row No. 1) has been reported and its crystal structure has been determined using a single-crystal X-ray diffraction method. The six above-listed ternary phases are also mentioned without any explanation on how to incorporate an additional phase into the earlier published phase diagram.

In the study by Simura *et al.*^[2], two alloys with the nominal compositions of $\text{Al}_{72}\text{Pd}_{18}\text{Co}_{10}$ and $\text{Al}_{74}\text{Pd}_{14}\text{Co}_{12}$ (marked as #1 and #2, respectively, in Fig. 1) were investigated. The composition of the *R*-phase in the solidified alloy #1 was measured as $\text{Al}_{72-73}\text{Pd}_{15-20}\text{Co}_{7-13}$ (shown as yellow region in Fig. 1), the Pd/Co ratio was found to decrease from the rim to the center of the grains. After heating at 1000 °C and subsequent cooling to 900 °C for 22 h (~4.5 °C/hour), the *R*-phase was found to be mainly replaced by the ϵ -phases (without mentioning their compositions). There was suggested that the *R*-phase has solidified from the liquid first and its compositional region is different from the above-mentioned nominal compositions. The other alloy, heated at 1050 °C and slowly cooled to 790 °C for 65 h (~4 °C/hour), contained a more homogeneous *R*-phase, measured composition of which was $\sim\text{Al}_{73}\text{Pd}_{13.5}\text{Co}_{13.5}$, i.e. close to the nominal one. The latter was used for the structural determination.

As can be seen in Fig. 1, both the nominal and measured compositions of the samples, studied by Simura *et al.*^[2], correspond to the overall ϵ -phase region. It should be emphasized that the Al–Co–Pd alloy system has been studied by Yurechko *et al.*^[1] on 90 alloys, annealed at 790, 940, 1000 and 1050 °C, and the isothermal sections constructed there do not leave a room for an additional

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phase in the studied temperature range. The results of the independent recent report on the Al–Co–Pd system by Černíková *et al.*^[3] are consistent with those published by Yurechko *et al.*^[1] and the revelation of the above-mentioned new *R*-phase was there ignored.

This gives a cue that the new reported Al–Co–Pd structure might belong to an already known ternary phase, crystal structure of which was just differently described. In order to check this suggestion, the powder XRD pattern, calculated using the structural model by Simura *et al.*^[2], was compared to the experimental XRD patterns of the earlier observed Al–Co–Pd phases. As can be seen in Fig. 2, the diffraction pattern of the *R*-phase indeed exhibits a great similarity to that of the *U*-phase, studied in more detail by Mi *et al.*^[4].

The *U*-phase^[4] was associated with a *C*-centered monoclinic structure with the unit cell parameters given in the row No. 3 of Table 1. Suggesting two different descriptions of the same compound, the powder XRD pattern, calculated from the data by Simura *et al.*^[2], was also successfully indexed using a *C*-centered monoclinic lattice. For the rhombohedral and corresponding monoclinic alternatives, the lattices parameters are given in Table 1 (see row No. 1 and No. 2, respectively). Within the precision typical of the powder X-ray diffraction, all and only 486 *specific* powder diffraction lines of the *R*-phase in the range of $2\theta = 5-90^\circ$ (for Co $K_{\alpha 1}$ radiation) were found also belonging to a *C*-centered monoclinic structure with the simulated unit cell parameters. As an example, the positions of the calculated powder diffraction lines in a small angular range are presented in Table 2 and Fig. 3a. The differences in the positions of the *specific* lines are not more than 0.001° , and the number of the corresponding reflections is the same for the both alternatives (i.e., four six-fold vs. six four-fold or two six-fold vs. three four-fold etc.). The simulated monoclinic unit cell parameters are close to those obtained experimentally^[4] and two of them are very close to those of the *R*-phase. Since the *U*-phase exhibits quite a wide compositional region, some differences in the unit cell parameters could also follow from some compositional differences (see, for example, row No. 5 vs. No. 3 in Table 1). However, for the experimentally determined unit cell parameters of the *U*-phase as in row No. 3 of Table 2, the calculated positions of the diffraction lines exhibit visible splitting apart from just shift following from some difference in the unit cell parameters (see Fig. 3c). Thus, instead of one specific line, expected for the rhombohedral structure, there could be up to six lines of the monoclinic structure, some of them not visible in the experimental diffraction pattern due to low intensities.

This phenomenological analysis can be supported by general considerations based on the space group relation of the alternative structures. The *U*-phase^[4] was reported to exhibit the systematic extinctions complying with the *C*1-1 extinction symbol, i.e., to belong to the space group *C*2 (No. 5), or *C**m* (No. 8), or *C*2/*m* (No. 12)^[5]. Although none of them has a group-subgroup relation to the space group $R\bar{3}$ (No. 148), concluded by Simura *et al.*^[2], the latter is one of the maximal *translationengleiche* subgroups of the space group $R\bar{3}m$ (No. 166), along with *C*2/*m*, the most symmetric of the three possible monoclinic lattices^[6]. Consequently, the corresponding basic vectors of *C*2/*m*, can be written as^[6]:

$1/3(2\mathbf{a}+\mathbf{b}-2\mathbf{c})$, \mathbf{b} , \mathbf{c} , where \mathbf{a} , \mathbf{b} and \mathbf{c} are the basic vectors of the rhombohedral $R\bar{3}m$ lattice.

The corresponding monoclinic unit cell parameters can be recalculated as following:

$$a_U = 1/3\sqrt{(3a_R^2 + 4c_R^2)}, b_U = a_R, c_U = c_R \text{ and } \beta_U = \sin^{-1}(2c_U/3a_U) + 90^\circ.$$

For $a_R = 2.91019$ nm and $c_R = 1.31854$ nm, this results in $a_U = 1.89625$ nm, $b_U = 2.91019$ nm, $c_U = 1.3185395$ nm and $\beta_U = 117.617^\circ$ indeed. The two other above-mentioned monoclinic space groups can be related to the $R\bar{3}m$ space group in a similar way, but only through intermediate structures:

$$R\bar{3}m \rightarrow R32 \rightarrow C2; R\bar{3}m \rightarrow R3m \rightarrow Cm.$$

The $R\bar{3}$ space group was concluded by Simura *et al.*^[2] through an analysis of the reflection conditions (identical for both $R\bar{3}$ and $R\bar{3}m$) and the intensity distribution. The effect of the differences among the $R\bar{3}$ and $R\bar{3}m$ space groups on the observed intensity distribution is probably minor. Since a high degree of chemical and/or geometrical disorder was noted there, the correctness of the symmetry evaluation and/or possibility of an addition/removal of the mirror planes normal to the $\langle 10\bar{1}0 \rangle$ (or $\langle 210 \rangle$) axes should be revisited.

In order to link between the results by Simura *et al.*^[2] and Mi *et al.*^[4], it is plausible to assign the space group $C2/m$ to the U-phase, which can also be described in the terms of the $R\bar{3}m$ pseudosymmetry.

These arguments support the suggestion that the R -phase reported by Simura *et al.*^[2] is in fact the differently described U-phase, revealed earlier. Unfortunately, the raw diffraction data for the U-phase^[1,4] are not available anymore and a reliable discrimination between the alternative structural proposals solely from the peak list was not possible. All 86 diffraction lines of the U-phase (those with $I/I_0 > 5\%$ are listed in Table 2 by Mi *et al.*^[4]) could also be indexed for a rhombohedral structure. Although the resulted average $\Delta 2\theta$ for a rhombohedral phase is larger (see row No. 4 vs. No. 3 in Table 1), this is quite a weak argument in favor of the monoclinic structure, since it has more total diffraction lines. Apart from the powder XRD diffractometry, the U-phase was also examined by electron diffraction in transmission electron microscope (TEM)^[4]. The $[001]$ electron diffraction pattern of the monoclinic U-phase was mentioned as being “surprisingly six-fold, but neither a hexagonal nor cubic lattice could be proved”. One could also suggest that the structure of the solidified U-phase¹ is rhombohedral and small changes resulting in the monoclinic structure could occur during the subsequent processing. In any case, the model by Simura *et al.*^[2] is applicable indeed.

The incongruent melting of the R -phase as well as a decrease of its melting temperatures with the decreasing Co concentrations, as reported by Simura *et al.*^[2], are indeed typical of the Al–Co–Pd U-phase^[1]. Therefore, during solidification, *higher*-Co concentrations are expected. The stability of the U-phase was confirmed at 790–1000 °C, while annealing at 1050 °C resulted in its melting^[1,4]. The F-phase is already solid at 1050 °C^[1] and the reaction $L+F \leftrightarrow \varepsilon+U$ is expected between 1020 and 1050 °C. Depending on the alloy composition, either U or ε can be the primary solidified phase. Under the conditions of the experiment, described by Simura *et al.*^[2], the primary formation of the U-phase, enriched by Co, is reasonable. Moreover, the U-phase extends along about constant Al composition, which is consistent with the reported observations^[2].

As to the composition, accepted for the R -phase^[2], it is quite far away from that required by its present identification. However, other information provided there, allows one to suggest quite inaccurate compositional measurement. Thus, a transformation resulting in the formation of the ε -phases, indeed expected in the studied alloys.

There is also a noticeable difference between the measured composition of the R -phase and that deduced from the model^[2]. The initial atomic model of the R -phase yielded the composition of $Al_{68.2}Pd_{23.6}Co_{8.2}$ (Al/Pd/Co = 450/156/54 in the unit cell, R_{prim} in Fig. 1) and the replacement of some Pd by Al and/or Co was suggested during its refinement. The final structural model yielded the $Al_{75.5}Pd_{16.3}Co_{8.2}$ composition (R_{ref} in Fig. 1). On the other hand, as it is well seen in Fig. 1, the Al concentration of the initial model is more realistic and, in order to get its correct composition, Pd should be mainly replaced by Co and not by Al. Thus, for example, ratio Al/Pd/Co = 458/108/94

¹ The starting temperature of 1050 °C applied by Simura *et al.*^[2] is above the melting temperature of the U-phase.

would result in $\text{Al}_{69.4}\text{Pd}_{16.4}\text{Co}_{14.2}$. A high degree of the chemical and/or geometrical disorder^[2], points, in fact, to partial occupancies of the suggested Wyckoff sites.

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Figure captions

Fig. 1. Overall compositions of the binary and ternary phases in the Al–Pd–Co system in the temperature range of 790–1050 °C (redrawn from Fig. 1 by Yurechko *et al.*^[1]). The nominal compositions of the alloys #1 and #2 by Simura *et al.*^[2], are labeled by the red squares; the compositions of the *R*-phase, measured in the alloy #1, is labeled by the yellow parallelogram. The primary composition of the *R*-phase ($R_{\text{prim.}}$) and its refined composition ($R_{\text{ref.}}$) are labeled by the blue squares. (The reader is referred to the web version of this paper for the color representation of this figure.)

Fig. 2. Powder XRD patterns (Co $K_{\alpha 1}$ radiation) of: a) the *R*-phase, as calculated from the model by Simura *et al.*^[2], b) the U-phase of the $\text{Al}_{69.1}\text{Pd}_{16.5}\text{Co}_{14.4}$ composition (redrawn from Fig. 2d by Yurechko *et al.*^[1]). (The reader is referred to the web version of this paper for the color representation of this figure.)

Fig. 3. a) Powder XRD pattern of the *R*-phase, calculated from the model by Simura *et al.*^[2], with the unit cell parameters listed in row No. 1 of Table 2 (red) and the expected positions of the diffraction lines of a hypothetical U-phase with the unit cell parameters shown in row No. 2 of Table 2 (pink).
b) Splitting of the diffraction lines of a hypothetical U-phase with a change of its unit cell parameters to $a = 1.896$, $b = 2.9105$, $c = 1.318$ nm and $\beta = 117.5^\circ$, which are only ~0.3% different from those in (a). c) Theoretical positions of the diffraction lines of the U-phase with the cell parameters refined from the experimental data (shown in row No. 3 of Table 2). In all simulations, the wavelength of the Co $K_{\alpha 1}$ radiation was used. (The reader is referred to the web version of this paper for the color representation of this figure).

Table 1Crystallographic data of the *R*-phase vs. U-phase.

No		S.G. or symmetry	Unit cell parameters				Refinement quality			
			<i>a</i> , nm	<i>b</i> , nm	<i>c</i> , nm	β , °	<i>V</i> , nm ³	$\Delta 2\theta_{aver}$, °	$\Delta 2\theta_{max}$, °	<i>FOM</i> (30)
1	<i>R</i> -phase ^[2]	R $\bar{3}$	2.91019	-	1.31854	-	9.671			
2	U-phase indexed from the data in row No. 1	C-center. monoclin.	1.89619	2.91010	1.31850	117.617	6.446	0.000	0.000	999.9
3	U-phase in Al _{69.1} Pd _{16.5} Co _{14.4} ^[4]	C-center. monoclin.	1.9024	2.9000	1.3140	117.26	6.444	0.012	0.033	7.9
4	<i>R</i> -phase indexed from the data in row No. 3	R $\bar{3}$	2.9071	-	1.3176	-	9.643	0.033	0.078	10.3
5	U-phase in Al _{69.5} Pd _{11.9} Co _{18.6} ^[4]	C-center. monoclin.	1.9021	2.8955	1.3121	117.22	6.426			

Table 2An example of the diffraction line positions of the *R* vs. U phases with the corresponding refined unit cell parameters (rows No. 1 vs. No. 2 in Table 1, Co K $_{\alpha 1}$ radiation). N is the multiplicity.

<i>R</i> -phase ^[2]						U-phase refined					
d, Å	2 θ , °	<i>h</i>	<i>k</i>	<i>l</i>	N	d, Å	2 θ , °	<i>h</i>	<i>k</i>	<i>l</i>	N
3.43344	30.202	1	4	3	6	3.43334	30.203	1	1	3	4
3.43344	30.202	4	1	3	6	3.43334	30.203	0	4	3	4
3.43344	30.202	-1	5	3	6	3.43334	30.203	-1	5	3	4
3.43344	30.202	-4	5	3	6	3.43334	30.203	-3	5	3	4
						3.43333	30.203	-4	4	3	4
						3.43333	30.203	-5	1	3	4
3.37836	30.706	6	2	1	6	3.37826	30.707	4	2	1	4
3.37836	30.706	-6	8	1	6	3.37825	30.707	-4	6	1	4
						3.37825	30.707	-2	8	1	4
3.33822	31.085	7	1	0	6	3.33812	31.086	5	1	0	4
3.33822	31.085	1	7	0	6	3.33812	31.086	3	7	0	4
						3.33811	31.086	2	8	0	4
3.32037	31.256	6	1	2	6	3.32028	31.257	3	1	2	4
3.32037	31.256	-6	7	2	6	3.32027	31.257	-4	6	2	4
						3.32027	31.257	-3	7	2	4
3.26851	31.765	1	0	4	6	3.26841	31.766	-2	0	4	2
						3.26841	31.766	-3	1	4	4