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A study of the Al-rich part of the Al–Ni–Pt alloy system

B. Grushko[a,*], D. Kapush[b], L. Meshi[c]

[a] PGI-5, Forschungszentrum Jülich, D-52425 Jülich, Germany
[b] I.N. Frantsevich Institute for Problems of Materials Science, 03680 Kyiv 142, Ukraine
[c] Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

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ABSTRACT

The Al–Ni–Pt phase diagram was studied in the compositional region from 50 to 100 at.% Al. Isothermal sections were determined at 1000, 900 and 790 °C. At 1000 °C the Al_2Pt phase was found to extend up to ~$Al_{53}Ni_{23}Pt_{24}$ composition, separating the (Al_3Pt_2) and (Al_3Ni_2) phase fields. Two ternary structures were revealed. The one forming between ~$Al_{75}Ni_3Pt_{22}$ and $Al_{75}Ni_9Pt_{16}$ is rhombohedral isostructural to $Al_{28}Ir_9$ and the other forming between ~$Al_{73}Ni_8Pt_{19}$ and $Al_{72.5}Ni_{18}Pt_{9.5}$ has an orthorhombic ε_6 structure typical of Al–Pd and Al–Rh.

1. Introduction

For reasons of practical interest, the Al–Ni–Pt phase diagram has mainly been studied in its low-Al part and at quite elevated temperatures (see Ref. [1–3]). The first published version of the Al–Ni–Pt ternary diagram in Ref. [1] included the 1060 °C isothermal section in the whole compositional region. No ternary phases were reported in this work. Several quite speculative details of this study were not confirmed in more recent work. For example, in Refs. [2,3] a wide extension of Al_2Pt was observed towards lower Al, which cuts the continuity between isostructural Al_3Ni_2 and Al_3Pt_2 suggested in Ref. [1]. In Ref. [4] also a ternary phase, isostructural to $Al_{28}Ir_9$, was recently revealed somewhat below 1100 °C at the $Al_{74}Ni_{7.2}Pt_{18.8}$ composition.

In the present contribution we report a study of the Al-rich part of the Al–Ni–Pt alloy system at 790 to 1000 °C. The experimental data for the boundary binary system Al–Ni are used from Ref. [5] and for Al–Pt mainly from Ref. [6]. The highest-Al Al–Pt phase, designated $Al_{21}Pt_5$ in Ref. [6], was reinvestigated in Ref. [7] where its structure was determined and the more appropriate formula Al_4Pt was asserted.

2. Experimental

Due to the high price of Pt the alloys were mainly produced from samples previously studied in Ref. [3]. These samples were mixed in specific proportions between them and with Al or Al–Ni alloys. Initial alloys of 2–5 g were produced by levitation induction melting in a water-cooled copper crucible under a pure Ar atmosphere. The purity of Al was 99.999%, of Ni 99.98%, and of Pt 99.9%. Parts of the solidified ingots inserted into the Al_2O_3 crucibles were thermally annealed under vacuum at 790, 900 and 1000 °C up to 235 h and subsequently water quenched. The annealed samples were studied by powder X-ray diffraction (XRD, Cu $K_{\alpha1}$ radiation was used), and scanning electron microscopy (SEM). The local phase compositions were determined in SEM by energy-dispersive X-ray analysis (EDX) on polished unetched cross sections. TEM examinations of selected samples were carried out on powdered materials dispersed on grids with carbon film.

3. Results and discussion

Below the Al_2Pt–Al_3Ni_2 line the constitution of the Al–Ni–Pt alloy system was not visibly different at 1000 °C from that at 1100 °C (see Fig. 1; for the comparison the relevant part of the diagram at 1100 °C is redrawn from Ref. [3] in Fig. 1a). The Al_2Pt phase was found to extend up to at least the $Al_{53}Ni_{23}Pt_{24}$ composition, separating the (Al_3Pt_2) and (Al_3Ni_2) phase fields. Below 1000 °C this compositional region was not studied.

Two ternary structures were revealed at higher Al concentrations. Their powder XRD patterns are shown in Fig. 2 together with the patterns of the neighboring binary phases, and their crystallographic data are included in Table 1. Both ternaries are formed between 1000 and 1100 °C. One is designated χ due to its similarity to the Al–Ir χ-phase (the latter is described in Ref. [8] and references therein). The detailed diffraction data of the Al–Ni–Pt χ-phase are provided in Ref. [4]. The powder X-ray diffraction pattern of the other ternary phase (Fig. 2b) recalls that of the Al–Ni–Ir ε-phase reported in Ref. [9]. Electron diffraction examinations (see Fig. 3a and b) revealed the ε_6 structure, also forming in Al–Rh and Al–Pd and dissolving a significant percentage of numerous transition elements (see Ref. [10] and references therein). The presence of the ternary χ-phase was also verified by electron diffraction, see Fig. 3c. The latter was found to be formed in a compositional region

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* Corresponding author. Tel.: +49 2461 612399; fax: +49 2461 616444.
E-mail address: b.grushko@fz-juelich.de (B. Grushko).

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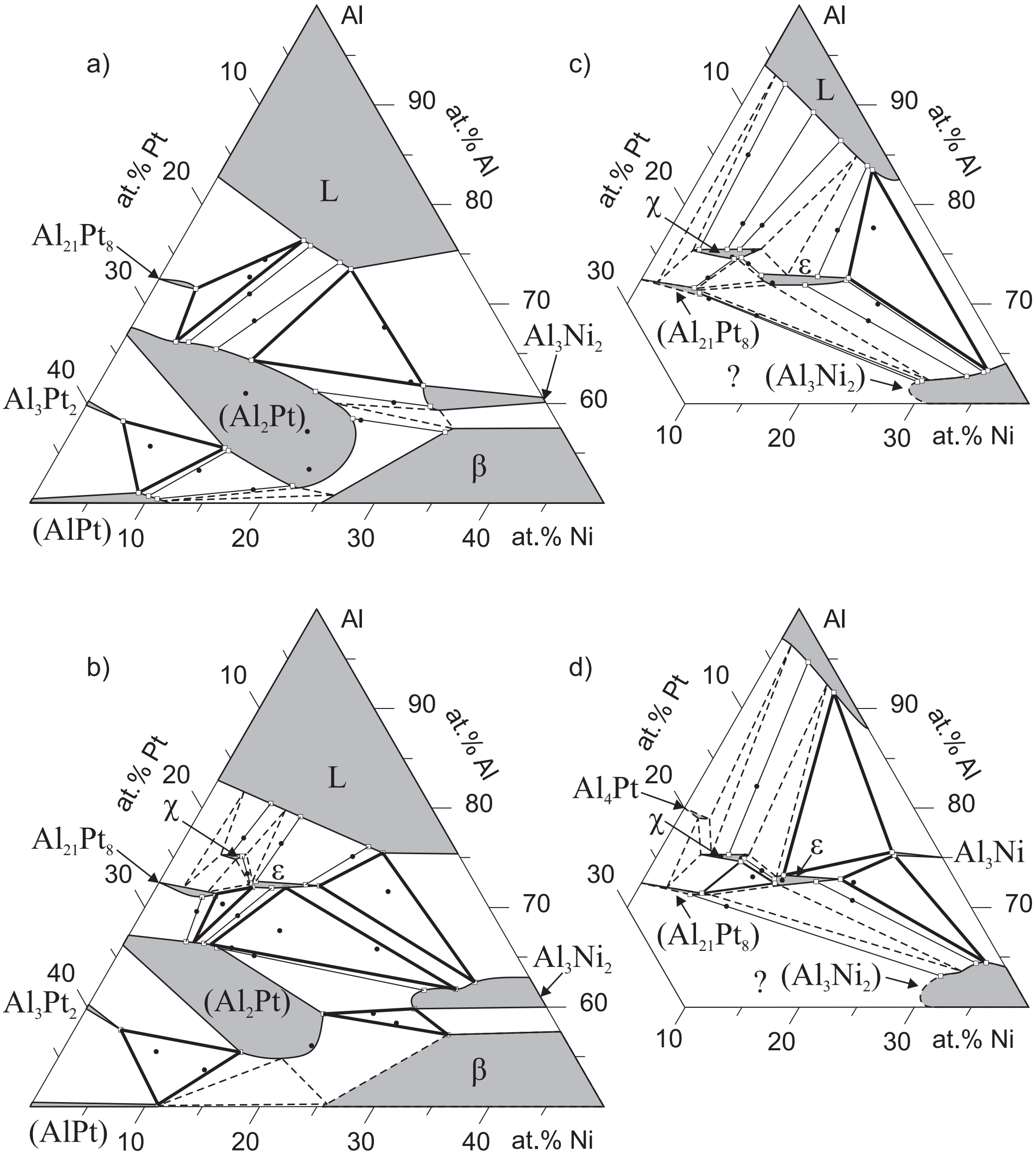

Fig. 1. Partial isothermal sections of Al–Ni–Pt at: (a) 1100 °C redrawn from Ref. [3], (b) 1000 °C, (c) 900 °C and (d) 790 °C. L is the liquid. The compositions of the studied samples are shown by spots. The compositions of the phases determined by SEM/EDX are shown by squares. Provisional tie-lines are shown by broken lines. The ranges where the equilibria were not clarified are marked by (?).

Table 1
Crystallographic data of the phases mentioned in the text and figures.

Phase	Space group	Lattice parameters			Composition, at.%			Reference
		a [nm]	b [nm]	c [nm]	Al	Ni	Pt	
Al_4Pt	$P3c1$	1.3077	–	0.96342	80	0	20	[7]
$Al_{21}Pt_8$	$I4_1/a$	1.297	–	1.065	72.4	0	27.6	[13]
		1.2911 (6)	–	1.0615 (8)	71	4	25	This work
Al_2Pt	$Fm\bar{3}m$	0.5920	–	–	66.7	0	33.3	[13]
		0.59411 (5)	–	–	53	23	24	This work
Al_3Pt_2	$P\bar{3}m1$	0.4208	–	0.5172	60	0	40	[13]
AlPt	$P2_13$	0.4864	–	–	50	0	50	[13]
		0.48202 (11)	–	–	51	10	39	This work
Al_3Ni	$Pnma$	0.6598	0.7351	0.4802	75	25	0	[5]
Al_3Ni_2	$P\bar{3}m1$	0.4028	–	0.4891	60	40	0	[5]
		0.4083 (6)	–	0.4984 (10)	60	30	10	This work
AlNi (β)	$Pm\bar{3}m$	0.2887	–	–	50	50	0	[5]
χ	$P31c$	1.20953	–	2.6932	74.0	7.2	18.8	[4]
ε	$Pna2_1$ or $Pnma$	2.34[a]	1.65[a]	1.24[a]	73	10.5	16.5	This work

[a] Electron diffraction data.

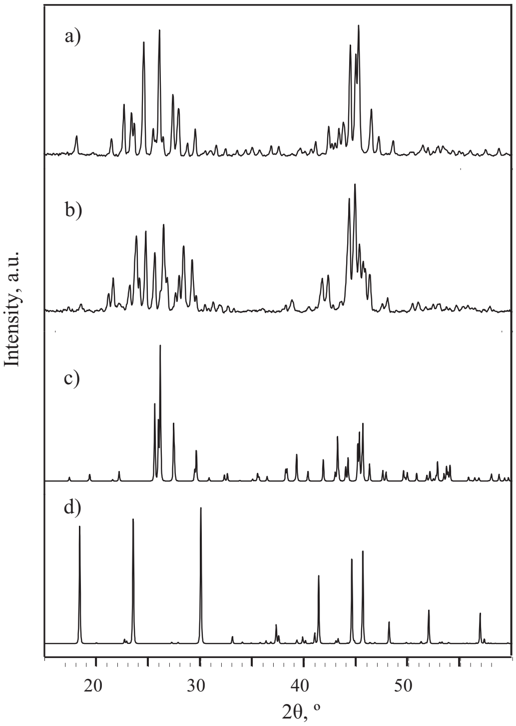

Fig. 2. Powder X-ray diffraction patterns (Cu $K_{\alpha 1}$-rad.) of the Al–Ni–Pt: (a) χ-phase, (b) ε-phase, compared to those of (c) $Al_{21}Pt_8$ (calculated from the data of 58137-ICSD) and (d) Al_4Pt (calculated from the data of Ref. [7]).

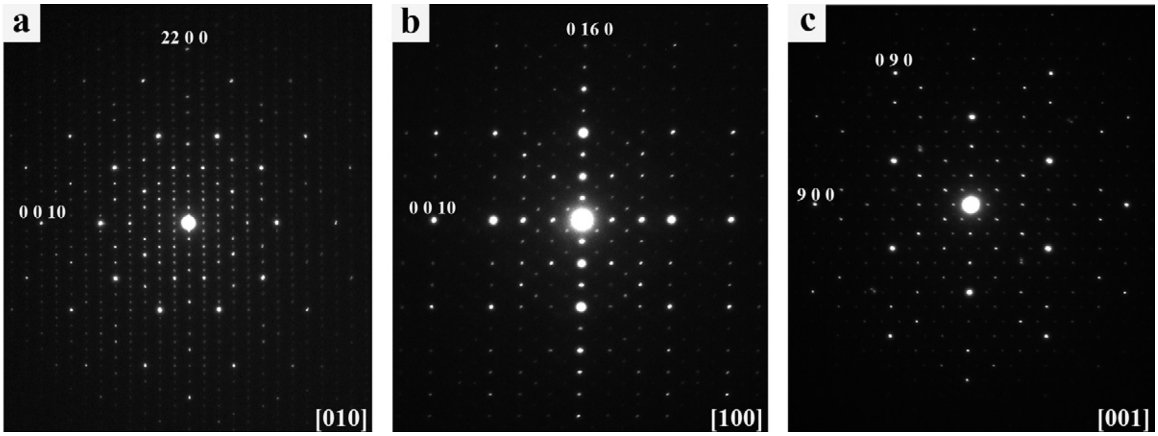

Fig. 3. Precession electron diffraction patterns taken from the ε-phase along: (a) the [0 1 0] and (b) [1 0 0] orientations, and from the χ-phase along the [0 0 1] orientation. The patterns were obtained with a precession angle of ~2° (34.9 mrad). Reflections with high d_{hkl} values, which appear close to the transmitted beam, are of a dynamical nature, thus some extra reflections are visible.

maximally extended between $Al_{75}Ni_4Pt_{21}$ and $Al_{75}Ni_6Pt_{19}$. The compositions of the ε-phase were found to extend from $Al_{73}Ni_8Pt_{19}$ to $Al_{72.5}Ni_{14}Pt_{13.5}$.

Above 60 at.% Al the ternary equilibria ε–(Al_2Pt)–($Al_{21}Pt_8$), ε–(Al_2Pt)–(Al_3Ni_2) and ε–(Al_3Ni_2)–L were determined from the investigation of the three-phase samples, and those of χ–($Al_{21}Pt_8$)–L, χ–($Al_{21}Pt_8$)–ε and χ–ε–L were established from the existence of the corresponding two-phase equilibria (see Fig. 1b).

At 900 °C the compositional regions of the ternary phases are somewhat wider than at 1000 °C (Fig. 1c). The χ-phase was found in a compositional region maximally extended from $Al_{75}Ni_3Pt_{22}$ to $Al_{75}Ni_9Pt_{16}$, and the ε-phase from $Al_{73}Ni_{10}Pt_{17}$ to $Al_{72.5}Ni_{18}Pt_{9.5}$. Instead of the ε–(Al_2Pt) equilibrium the ($Al_{21}Pt_8$)–(Al_3Ni_2) equilibrium was observed. The ternary equilibria ε–(Al_3Ni_2)–L and ($Al_{21}Pt_8$)–(Al_2Pt)–(Al_3Ni_2) were determined from the investigation of the three-phase samples, and those of χ–($Al_{21}Pt_8$)–L, χ–($Al_{21}Pt_8$)–ε, χ–ε–L and ($Al_{21}Pt_8$)–ε–(Al_3Ni_2) were established from the existence of the corresponding two-phase equilibria (see Fig. 1c).

With the temperature decrease two additional binary phases are involve in equilibria. The Al_3Ni phase is formed below 854 °C [5] and Al_4Pt below 806 °C [6]. Investigation of Al-rich alloys at 790 °C revealed the equilibria presented in Fig. 1d. The extension of the Al_4Pt phase into the ternary compositional range was not determined at this temperature, but in as-cast alloys this phase was found to contain up to 6.5 at.% Ni. Therefore it is plausible that at 790 °C its compositional region is sufficiently wide to prevent the L–($Al_{21}Pt_8$) equilibrium at lower Ni concentration, while at higher Ni concentration this is not possible due to the extension of the χ-phase. Therefore the χ–(Al_4Pt)–($Al_{21}Pt_8$) equilibrium is suggested.

It is worth noting that a structure associated with the χ-phase was earlier observed by electron diffraction in Ref. [11] in a rapidly solidified Al_5Pt alloy. This observation was confirmed in Ref. [12] where the same electron diffraction patterns were obtained from materials formed by the annealing of subsequent Al and Pt layers. In both Refs. [11,12], these diffraction patterns were associated with a metastable phase and not included in the equilibrium Al–Pt phase diagram. Together with these observations our experiments point to the stabilization of a metastable Al–Pt χ-phase by Ni. Extrapolation of the region of the ternary χ-phase towards the Al–Pt terminal results in a composition close to Al_3Pt, i.e. quite similar to the composition of the Al–Ir χ-phase determined in Ref. [8]. This composition rather than Al_5Pt reported in Ref. [11] is correct.[1]

In contrast to the χ-phase, no Al–Pt metastable phase was associated in the literature with any of the ε-structures. The description of the second metastable structure observed in the Al–Pt system in Ref. [12] is not sufficiently detailed but probably does not confirm an ε-phase formation. Also a metastable phase with unclear structure, reported in Ref. [13] to be observed in splat-cooled samples and designated Al_3Pt(m), could rather be the χ-phase. However, the existence of a metastable Al–Pt ε-phase would not be very surprising, since, as already mentioned above, such structures are formed in Al–Pd. Both Pd and Pt belong to the same

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[1] Actually, Al_5Pt was mentioned to be an alloy composition, and the alloy also contained other phases. Therefore, the metastability of this binary structure is not obvious from the experiments presented in Ref. [11], and the same conclusion concerning the Al–Ir χ-phase was incorrect (see Ref. [8] for details).

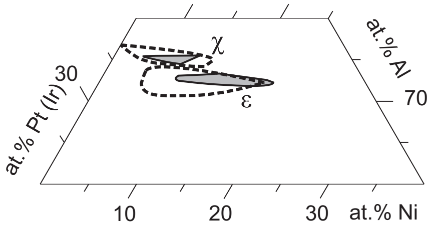

Fig. 4. Overall compositions of the χ and ε phases in Al–Ni–Ir (broken lines) and Al–Ni–Pt (filled).

column of the periodic table and contain isostructural phases at Al_4TM and $Al_{21}TM_8$ (TM = Pd or Pt). In Al–Pd the high-temperature ε-phases are formed at compositions including that of the low-temperature $Al_{21}Pd_8$ phase (see Ref. [14]). This would also be a composition expected for a metastable Al–Pt ε-phase. It has a slightly lower Al concentration than the χ-phase, which is in agreement with their ternary compositional regions. Therefore, the formation of the ternary ε-phase could also be an example of the stabilization of a binary metastable phase by Ni. The stabilization of a metastable ε-phase was already suggested in Al–Ni–Ir, where it is stable in a compositional region extending from $Al_{73}Ni_4Ir_{23}$ to $Al_{72}Ni_{17.5}Ir_{10.5}$ (see Ref. [9]). The compositional regions of the χ and ε phases in Al–Ni–Ir and Al–Ni–Pt are compared in Fig. 4.

4. Conclusions

We report a study of the Al–Ni–Pt alloy system in a compositional range of above 50 at.% Al. Partial 1000, 900 and 790 °C isothermal sections were constructed. At 1000 °C the Al_2Pt phase extends up to ~$Al_{53}Ni_{23}Pt_{24}$ composition, separating the (Al_3Pt_2) and (Al_3Ni_2) phase fields. The phase equilibria involve two ternary phases χ and ε, maximally extended between ~$Al_{75}Ni_3Pt_{22}$ and $Al_{75}Ni_9Pt_{16}$ and between ~$Al_{73}Ni_8Pt_{19}$ and $Al_{72.5}Ni_{18}Pt_{9.5}$, respectively.

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