Phase relations in the Al–Ta system: on the translational symmetries of a triclinic structure and a new hexagonal giant cell structure

Stefan Mahne [a], Bernd Harbrecht [a,*], Frank Krumeich [b]

[a] Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany
[b] Arbeitsgemeinschaft Festkörperanalytik, Universität Bonn, Römerstr. 164, D-53117 Bonn, Germany

Abstract

The translational symmetries of two structurally complex phases of the Al–Ta system were determined by means of X-ray and electron diffraction methods. The thermal stability ranges of the phases were delimited and the phase relations in the medium range of the Al–Ta system were unravelled: Al_uTa ($u \approx 1.5$), triclinic, aP*, $a = 1074.8(3)$ pm, $b = 1107.8(4)$ pm, $c = 1043.3(4)$ pm, $\alpha = 90.45(2)°$, $\beta = 97.60(2)°$ and $\gamma = 63.19(2)°$, is stable below about 1500 K and decomposes in the solid state to yield entropically stabilized $Al_{69}Ta_{39}$ (cF432) and Al_vTa ($v \approx 1.4$), hexagonal, hP*, $a = 3214(2)$ pm and $c = 1341(1)$ pm. Al_vTa itself transforms in a peritectoid reaction above about 1620 K into $Al_{69}Ta_{39}$ and Al_wTa ($w \approx 1.0$) of monoclinic symmetry.

Keywords: Phase relations; Aluminium; Tantalum; Thermal stability

1. Introduction

In a first step of a preparative and structural reinvestigation of tantalum aluminides we determined the translational symmetries of two phases in the Al_3Ta–σ-$AlTa_x$ section of the binary system by means of X-ray and electron diffraction methods [1]. Furthermore, we performed a structure analysis of a phase, the composition of which turned out to be $Al_{69}Ta_{39}$ [2]. The atomic environments in the cubic giant cell structure of $Al_{69}Ta_{39}$ represent interesting combinations of Frank–Kasper-type and b.c.c. coordinations.

These results motivated further studies of the phase relations of other insufficiently characterized and new Al–Ta phases which we found in the course of the systematic investigation. Subjects of this report are a phase of triclinic symmetry previously termed "l.t.-Al_3Ta_2" of suggested orthorhombic symmetry [3] and a hitherto unmentioned phase with a huge hexagonal unit cell offering space for more than 700 atoms. In the present contribution we want to supplement the information about the phases and their relations in the medium range of the system.

In view of the size of the unit cells and the previous confusion concerning the composition of $Al_{69}Ta_{39}$ [1–6], assignments of stochiometric formulae to phases of unknown structure are avoided. The distinct phases will tentatively be termed Al_uTa (aP*), Al_vTa (hP*) and Al_wTa (mP*, equivalent to "AlTa" in Refs. [1,6]) until their crystal structures are solved.

2. Experimental details

Details of synthesis by arc melting and reaction of compacted mixtures of elemental Al and Ta powders in Ta ampoules (electrical resistance furnaces) are given in Ref. [1]. The Al–Ta compounds described in this contribution were obtained both by annealing of as-cast samples and by reaction of the elemental components below the temperature of peritectoid decomposition.

X-ray powder diffractograms, Guinier photographs and electron diffraction patterns were recorded and processed as described in Ref. [1]. High resolution transmission electron microscopy (HRTEM) images and convergent beam electron diffraction (CBED) patterns were obtained with a CM30 instrument (Philips, Eindhoven, Netherlands) working at 300 kV.
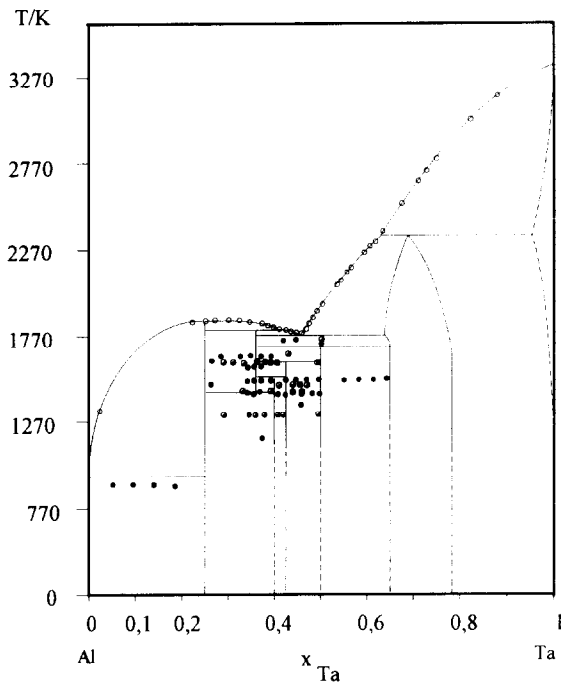
* Corresponding author.

Fig. 1. Compositions and reaction temperatures of the prepared samples shown in a revised phase diagram [8]: open circles, as-cast samples; half-filled circles, annealed samples after arc melting; filled circles, solid state reactions in sealed Ta ampoules.

In order to get an estimate of the error in the compositions of the phases, the nominal compositions of more than 20 samples, the Guinier photographs of which showed the diffraction patterns of the respective phases, were taken into account. Therefore the error $\delta(x_{Ta})$ is assumed to be less than 0.05. At temperatures higher than 1500 K and after reaction times of several weeks, loss of Al due to slow evaporation was observed (cf. Ref. [7]). Temperatures of the reactions were controlled by PtRh–EL18 and NiCr–Ni thermocouples located 1–2 cm away from the reaction ampoules. The deviation between measured and real temperatures is estimated to be less than 50 K. Conservation of the high temperature phases after quenching of the samples is assumed. Fig. 1 gives information on the reaction conditions of the experiments.

3. The triclinic phase Al_uTa $(u \approx 1.5)$

According to Schuster [3], "$h.t.$-Al_3Ta_2", which turned out to be $Al_{69}Ta_{39}$ [2], transforms into "$l.t.$-Al_3Ta_2" below 1498 K. In the present investigation, annealing of $Al_{69}Ta_{39}$ ($x_{Ta} = 0.36$, as cast, 1420 K, 20 days) resulted in a mixture of Al_3Ta and another phase, Al_uTa. A part of the corresponding diffractogram is shown in Fig. 2. The Bragg angles and intensities for Al_uTa are consistent to a large extent with those of Schuster's "$l.t.$-Al_3Ta_2" of supposed orthorhombic symmetry.

There is no access to Al_uTa by melting techniques, but it is formed by the peritectoid reaction of $Al_{69}Ta_{39}$
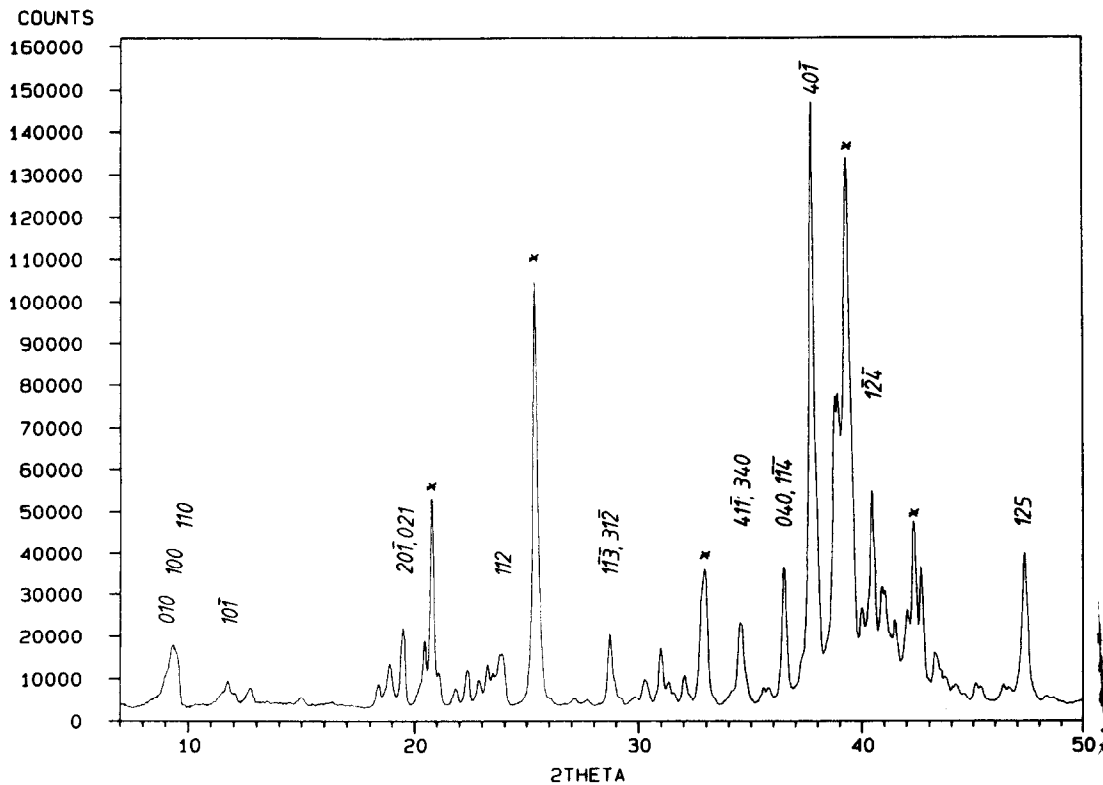

Fig. 2. Part of an X-ray diffractogram of peritectoidally decomposed $Al_{69}Ta_{39}$: Al_uTa (selected reflections are labelled) and Al_3Ta (reflections are indicated by asterisks).

Table 1

Powder diffraction of Al_uTa ($2\theta \leqslant 40.9°$): Cu Kα radiation, indices for Al_uTa, aP*, $a = 1074.8(3)$ pm, $b = 1107.8(4)$ pm, $c = 1043.3(4)$ pm, $\alpha = 90.45(2)°$, $\beta = 97.60(2)°$ and $\gamma = 63.19(2)°$

Sin² θ×10⁵		h k l					I_{rel}
Observed	Calculated						
610	609	0	1	0			1
658	658	1	0	0			6
695	692	1	1	0			10
1041	1041	1	0	−1			4
1097	1097	0	1	1			2
1235	1234	0	1	−1			3
2543	2536, 2540	1	0	−2, 1	2	1	3
2683	2700	0	1	2			6
2851	2841, 2857	2	0	−1, 0	2	1	10
3133	3132	1	1	2			6
3577	3584	1	−1	−2			3
3746	3757	2	1	−2			5
4164	4162	2	0	−2			4
4268	4244, 4248	1	−2	0, 1	2	2	8
5484	5481	0	3	0			1
6133	6125, 6125	1	−1	−3, 3	1	−2	7
6248	6242, 6260	0	3	−1, 2	1	−3	1
6614	6602	2	3	−2			1
6814	6840	1	2	−3			3
7118	7109	3	3	1			6
7286	7299	0	3	2			2
7597	7581	1	−1	3			3
7941	7947, 7948	2	1	3, 3	1	2	9
8601	8626	2	−2	−2			1
8779	8770, 8771	4	1	−1, 3	4	0	10
8900	8907	0	0	4			2
9245	9244	0	1	4			5
9414	9409	3	−1	1			4
9758	9744, 9779	0	4	0, 1	−1	−4	23
10159	10144, 10159, 10168	2 0 −4, 2 4 2, / 4 3 1					3
10418	10393	4	0	−1			100
11018	11006	1	2	4			46
11118	11105	0	3	−3			25
11683	11671, 11695	3	−1	2, 4	2	−3	9
11919	11908	1	−2	−4			31
12194	12202	3	3	3			16

and a phase richer in Ta, Al_vTa, below about 1500 K. Almost single-phase samples are obtained from cold-pressed mixtures of the elements ($x_{Ta} = 0.40(5)$, Ta ampoules, e.g. 1420 K, 3 days).

Taking into account the experimental error $\delta(x_{Ta}) = 0.05$, the phase is designated as Al_uTa with $u \approx 1.5$ here. Most of the 28 samples ($0.35 \leqslant x_{Ta} \leqslant 0.45$) prepared at 1370, 1420 and 1470 K also contained the neighbouring phase Al_vTa ($v \approx 1.4$; see Section 4) of similar composition.

Powder diffraction patterns of Al_uTa could be conclusively indexed triclinically with the help of the indexing routine TREOR [9]. The refined cell parameters are $a = 1074.8(3)$ pm, $b = 1107.8(4)$ pm, $c = 1043.3(4)$ pm, $\alpha = 90.45(2)°$, $\beta = 97.60(2)°$ and $\gamma = 63.19(2)°$; $V = 1100(6) \times 10^6$ pm³ (46 reflections, $2\theta_{max} = 47.3°$) (Fig. 2 and Table 1).

This unit cell was corroborated by electron diffraction. None of 25 different zone axes showed any point symmetry higher than $\bar{1}$. Fig. 3 provides the electron diffraction patterns of three reciprocal layers. The angles α^*, β^* and that between b^* and $[-101]^*$ are in good agreement ($\pm 0.5°$) with those calculated from the real cell parameters given above.

Based on the dependence of the mean atomic volume V_s on the mole fraction x_{Ta}, a value of $V_s(x_{Ta} = 0.4) = 16.4 \times 10^6$ pm³ can be estimated. The unit cell volume $V = 1100 \times 10^6$ pm³ is compatible with about 68 atoms in the cell. The phase width is delimited to a value $\Delta x_{Ta} < 0.02$ by comparison of the lattice parameters of samples containing different neighbouring phases; see also Ref. [1].

4. The hexagonal phase Al_vTa ($v \approx 1.4$)

In the course of the preparative investigations aiming at the synthesis of Al_uTa, a so far unknown, complex diffraction pattern appeared repeatedly. Two doublets
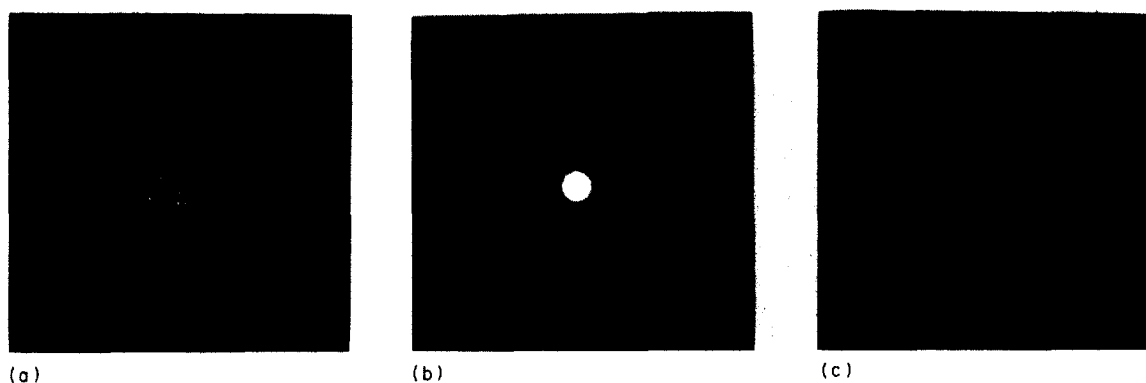

(a)   (b)   (c)

Fig. 3. Electron diffraction patterns of Al_uTa for various zone axes B: (a) $B = |010|$, zero layer a^*c^*; (b) $B = [100]$, zero layer a^*b^*; (c) $B = [101]$.
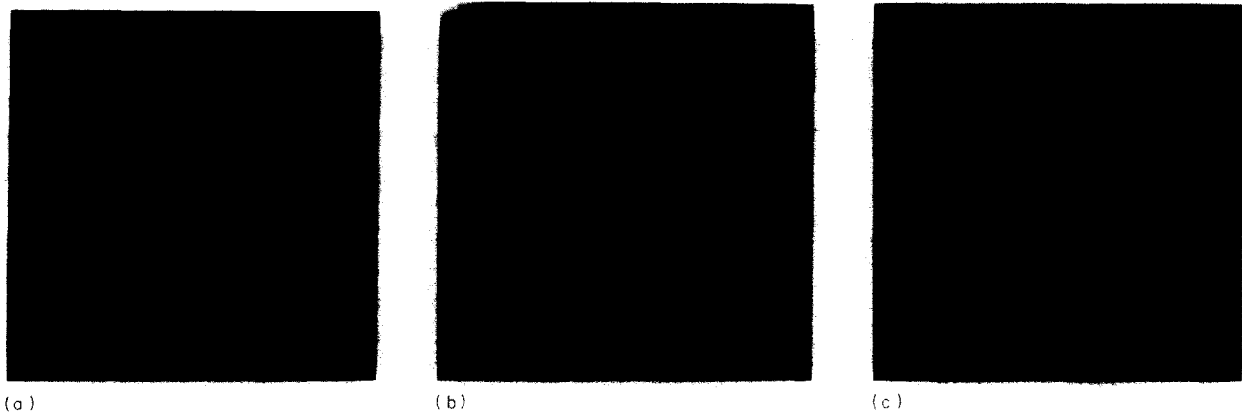
Fig. 4. Electron diffraction patterns of Al_vTa for various zone axes B: (a) $B = [010]$, zero layer a^*c^*; (b) $B = [1\ -1\ -1]$, ZOLZ and HOLZ (zero-order and higher-order Laue zones); (c) $B = [001]$, zero layer a^*b^*.

at low diffraction angles of $2\theta = 6.4°$, $7.3°$ and $9.1°$, $9.5°$ (Cu $K\alpha_1$) are characteristic for a phase which is described here for the first time. It will tentatively be called Al_vTa.

Like Al_uTa, Al_vTa does not form from the melt. It was obtained free of impurities by reaction of the elements ($x_{Ta} = 0.42$, Ta ampoule, 1420 K, 3 days). In the temperature range $1420 \leqslant T \leqslant 1570$ K and at compositions $0.38 \leqslant x_{Ta} \leqslant 0.47$, mixtures containing Al_vTa and $Al_{69}Ta_{39}$, triclinic Al_uTa or monoclinic Al_wTa are formed. The phase decomposes at about 1620 K to yield $Al_{69}Ta_{39}$ and Al_wTa. The composition Al_vTa, $v \approx 1.4$, follows from the evaluation of Guinier photographs of 24 samples containing Al_vTa prepared under distinct reaction conditions.

The primitive hexagonal unit cell of this new phase with axes of $a \approx 3.2$ nm and $c \approx 1.3$ nm was derived from electron diffraction patterns; see Fig. 4.
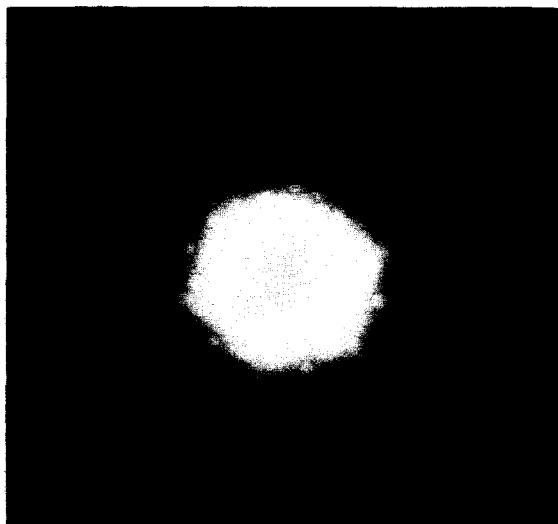

Fig. 5. CBED pattern of Al_vTa along $B = [001]$; the arrow points at the diffuse FOLZ (first-order Laue zone) exhibiting $6mm$ symmetry.

Table 2
Powder diffraction of Al_vTa ($2\theta \leqslant 31.5°$): Cu $K\alpha$ radiation, indices for Al_vTa, hP^*, $a = 3214(2)$ pm and $c = 1341(1)$ pm; I_{rel} refers to $I = 100$ ($2\theta = 39.22°$)

$\mathrm{Sin}^2\ \theta \times 10^5$		$h\ k\ l$	I_{rel}
Observed	Calculated		
307	306	2 0 0	2
406	406	1 0 1	1
633	636	2 0 1	2
690	689	3 0 0	2
1339	1325	3 1 1	3
1606	1608	4 1 0	1
1784	1785	3 2 1	4
1918	1914	5 0 0	1
2239	2238	2 2 2	7
2757	2756	6 0 0	5
2996	2986	5 2 0	3
3065	3046	1 0 3	2
3159	3163	4 3 1	3
3229	3234	5 0 2	11
3257	3276	2 0 3	3
3313	3316	5 2 1	6
3467	3463	4 2 2	3
3762	3751	5 3 0, 7 0 0	5
4287	4306	5 2 2	13
4375	4364	7 1 0	3
4600	4612	6 1 2	1
4688	4694	7 1 1	1
4833	4823	6 3 0	7
5003	5000	5 4 1	2
5056	5037; 5070	3 3 3; 7 0 2, 5 3 2	7
5145	5153	6 3 1	1
5514	5509	1 1 4	1
5747	5742	5 5 0	4
6102	6072	5 5 1	4
6211	6198, 6201, 6220	2 2 4, 9 0 0, 8 0 2	1
6364	6378	7 3 1	3
6674	6644	4 4 3	3
6965	6967	6 5 0, 9 1 0	2
7095	7120	7 4 0	2
7339	7333, 7346	7 1 3, 3 3 4	2

Convergent beam electron diffraction along c showed the hexagonal symmetry for the structure (Fig. 5).

The powder diffractogram shown in Fig. 6 was indexed on the basis of this hexagonal cell. Refinement of the lattice parameters (35 reflections, $2\theta_{max} = 31.5°$) (Table 2) resulted in $a = 3214(2)$ pm and $c = 1341(1)$ pm; $V = 11996(14) \times 10^6$ pm^3.

The interpolated mean atomic volume $V_s(x_{Ta} = 0.4) = 16.4 \times 10^6$ pm^3 is consistent with a unit cell content of about 730 atoms. According to a highly structured periodic pattern, seen in the HRTEM image taken along c (Fig. 7), the structure seems to be comprised of cluster-like units. Considering the lattice parameters of samples containing different neighbouring phases, the phase width is suggested to be less than $\Delta x_{Ta} = 0.01$.

Finally, we want to point out that there is a metric relation between Al_vTa and $Al_{69}Ta_{39}$: $d_{100}(Al_vTa) = 2748$ pm ≈ 2 $d_{110}(Al_{69}Ta_{39}) = 2 \times 1355$ pm. In addition, the zero-layer precession photograph along [001] of a twinned crystal of Al_vTa shows some similarity to the X-ray intensity modulation of the zero layer of $Al_{69}Ta_{39}$ along [111].

Fig. 7. HRTEM image of Al_vTa, $B = [001]$; the unit cell is marked by a frame.
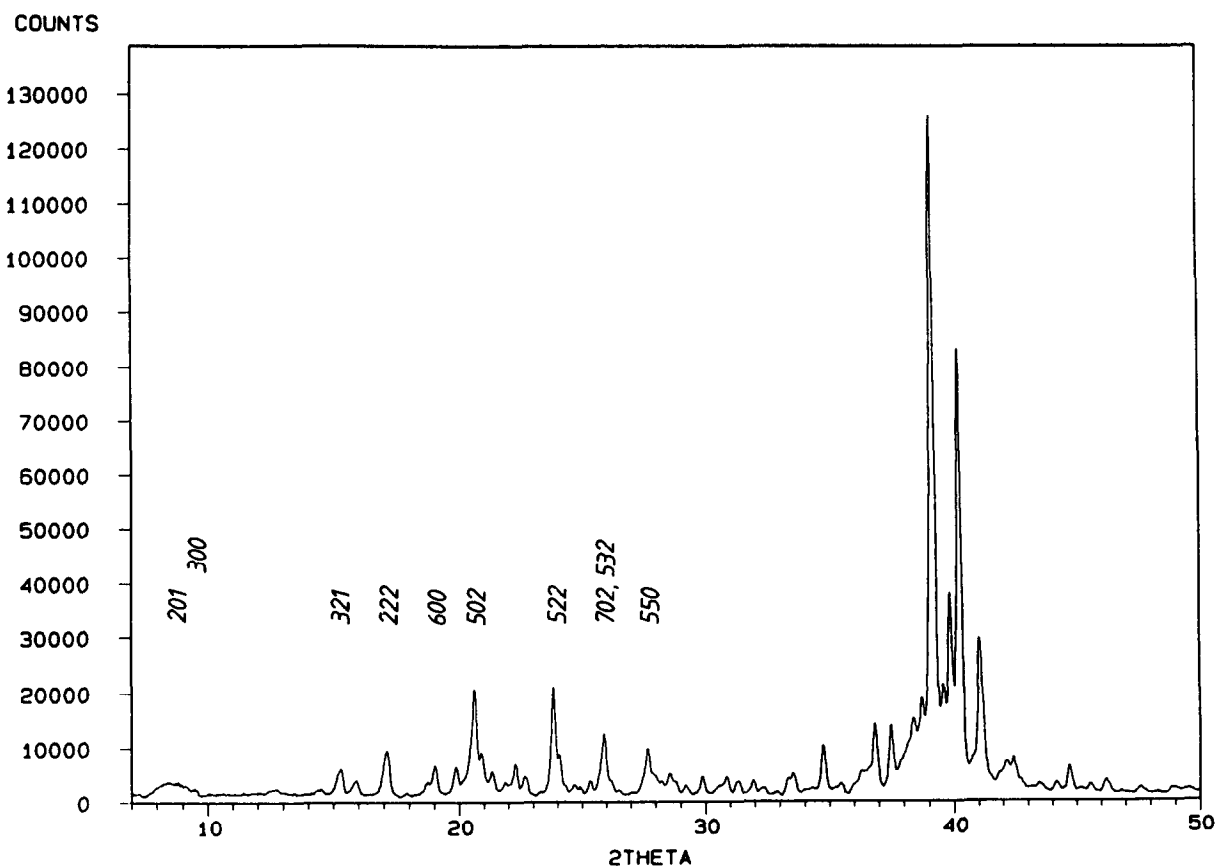

Fig. 6. Part of an X-ray diffractogram of Al_vTa (selected reflections are labelled).

5. Conclusions

The results of this study prove that the phase relations in the range between Al_3Ta and σ-$AlTa_x$ of the Al–Ta system are significantly more complex than previously thought. (i) The triclinic phase Al_uTa ($u \approx 1.5$) — assumed to be the low temperature modification of cubic $Al_{69}Ta_{39}$ — is richer in tantalum than the cubic phase and forms in a peritectoid reaction. (ii) The second phase involved in this reaction, Al_vTa ($v \approx 1.4$), contains more than 700 atoms in the hexagonal unit cell and seems structurally to be the most complex phase of the system. It also disproportionates in the solid state to yield $Al_{69}Ta_{39}$ and the aluminium-rich neighbour of σ-$AlTa_x$, monoclinic Al_wTa.

Acknowledgements

References

[1] S. Mahne, F. Krumeich and B. Harbrecht, *J. Alloys Comp.*, *201* (1993) 167.

[2] S. Mahne and B. Harbrecht, *J. Alloys Comp.*, *203* (1994) 271.

[3] J.C. Schuster, *Z. Metallkd.*, *76*(11) (1985) 724.

[4] A. Raman, *Aluminium (Duesseldorf)*, *41*(5) (1965) 318.

[5] K. Girgis and A.B. Harnik, *Naturwissenschaften*, *57* (1970) 242.

[6] P.R. Subramanian, D.B. Miracle and S. Mazdiyasni, *Metall. Trans. A*, *21* (1990) 539.

[7] H.F. Franzen and S. Schmidt, *J. Less-Common Met.*, *116* (1986) 73.

[8] B. Harbrecht and S. Mahne, in preparation.

[9] P.E. Werner, TREOR, *Trial and Error Program for Indexing of Unknown Powder Patterns*, University of Stockholm, 1988.