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Non-equilibrium phases in Al-rich Al-Pt alloys

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The solid solubility of Pt in Al was extended from 0 to 2 at. % by "two-piston" quenching technique. The stability of the Al-Pt solid solution during annealing is discussed. During the decomposition an intermediate metastable phase was detected, the unit cell constants of which were determined.

1. Introduction

Since Duwez [1] developed his "gun" technique of rapid quenching from the liquid state (now denoted liquisol-quenching [2]) investigations of the solid solubility of transition elements in aluminium have shown that even in the cases where equilibrium solubility is practically negligible (e.g. Al-Fe, Al-Co, Al-Ni, Al-Mo, Al-Pd, Al-W; [2]) extensive metastable solid solubility can be obtained. One of the rare binary alloys based on Al not investigated hitherto is Al-Pt. The present paper reports on experiments designed to determine metastable and terminal phases appearing in Al-Pt alloys on liquisol-quenching.

2. Results

Al-rich Al-Pt alloys (of up to 3 at. % Pt) were liquisol-quenched from 1200° C by means of the two-piston quenching technique and examined by X-ray diffraction analysis using a Debye-Scherrer camera of 114.6 mm for precise lattice parameter measurements, and a Nonius Guinier-de Wolf quadruple focusing camera for phase analysis. The experimental methods were identical with those reported in previously published papers [3-6].

2.1. As-quenched samples

According to Shunk [7], Pt appears to be insoluble in Al, and Al_4Pt, the most Al-rich equilibrium intermediate phase, exists at 20 at. % Pt. However, by liquisol-quenching we were able to obtain metastable supersaturated Al-solid solutions (α-Al) of up to about 2 at. % Pt. This metastable solubility extended to concentrations beyond the eutectic composition which on the equilibrium phase diagram is found at 1.0 at. % Pt.

The metastable solubility of Pt in Al was determined by measuring the α-Al lattice parameters of those samples which on X-ray films gave no other lines except those of α-Al, i.e. only when the samples were thinner than 10 μm and with no more than 2 at. % Pt (see Table I). The high-angle diffraction lines were diffuse

TABLE I Estimated distribution of phases at room temperature in Al-Pt alloys quenched from the melt

At. % Pt	Sample thickness (μm)	α-Al	Al_4Pt	ϵ (metastable)
0.5 to 2	10	0	—	—
	10 to 20	0	vw	m
	20 to 60	—	w or m	s
2 to 3	10	θ	m	s
	10 to 60	—	s	m
1.4 (Water-quenched)	Filings	—	vs	—

vw, very weak; w, weak; m, medium; s, strong; vs, very strong;—, absent; 0,α-Al solid solution; θ, α-Al solid solution with a smaller Pt content than that contained in the original melt.

and doublets unresolved, which indicated large distortions of the aluminium matrix. The respective results are presented in Fig. 1. Extrapolation of the linear variation of the α-Al lattice parameter with concentration gives a value of approximately 2.2 at. % as the limit of the metastable solubility of Pt in Al obtained with our quenching apparatus.

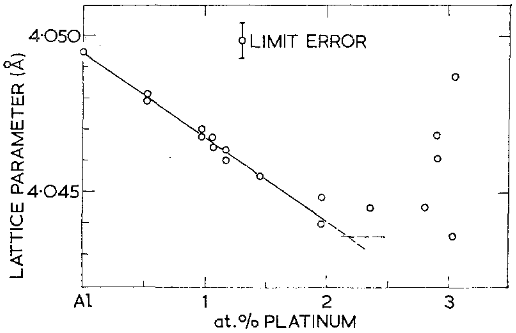

Figure 1 Lattice parameter of α-Al in Al-Pt alloys (samples thinner than 10 μm) plotted versus Pt concentration.

Thicker samples, 10 to 20 μm, contained no Al_4Pt phase, or hardly detectable amounts, together with a new and more marked phase of unknown structure (henceforth denoted "ε-metastable"). On the X-ray diffraction patterns, the lines of the ε-metastable were diffuse in comparison with the lines of Al_4Pt. However, the lattice parameters of α-Al in these thicker samples were increased in relation to the samples which were thinner than 10 μm, but were still below the parameter of pure aluminium, which would mean that there was still a certain proportion of Pt atoms in the solid solution.

The lattice parameter of α-Al in the samples thicker than 20 μm was equal to that of pure Al, i.e. there was no longer any Pt in solution, but large amounts of Al_4Pt and ε-metastable were present (Fig. 2a). In this case the diffraction lines of ε and α-Al were no longer diffuse and doublets of high-angle diffraction lines were resolved.

In water-quenched samples (the molten alloy was ejected directly into water) only the Al_4Pt phase was present with no traces of the ε-metastable phase.

For alloys with a Pt content exceeding 2 at. %, no sample containing α-Al exclusively was obtained, the Pt content of the solution varied greatly from sample to sample (Fig. 1), and large amounts of Al_4Pt and ε-phases were always present.

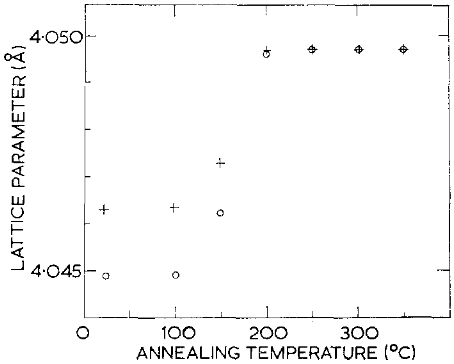

Figure 3 Change of lattice parameter of α-Al with annealing temperature after annealing for 15 min at several temperatures up to 350°C: O, Al-1.95 at. % Pt; +, Al-1.06 at. % Pt.

2.2. Annealing

Six α-Al samples with different Pt content were isochronously annealed for 15 min at temperatures from 100 to 650°C (with intervals of 50 or 100°C). The results obtained with two of these are shown in Fig. 3. α-Al decomposed between 100 and 200°C. No lines of any phase precipitated in the decomposition process could be detected on X-ray patterns up to 250°C. High-angle α-Al lines were diffuse up to 300°C, when doublets became resolved and lines of the Al_4Pt and ε-phases appeared, to become sharper at 400°C. At 500°C, lines of ε began to disappear,

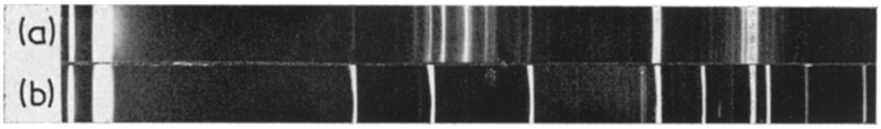

Figure 2 X-ray diffraction patterns of liquisol-quenched Al-1.95 at. % Pt (sample 35 μm thick): (a) immediately after quenching, showing reflections of α-Al, Al_4Pt and ε; (b) after isochronal annealing up to 650°C, showing reflections of Al and Al_4Pt.

while those belonging to Al_4Pt became more intense. At 650°C only the terminal Al and Al_4Pt were present (Fig. 2b).

Two α-Al samples with Pt contents of 0.51 and 1.43 at.% were isothermally annealed at 200°C. After annealing for 2 h, X-ray patterns showed highly diffuse diffraction lines which practically merged with the background in places where lines of ϵ-phase subsequently appeared. Twenty hours later, slightly broadened lines of Al_4Pt and ϵ-phases began to appear. With further annealing there was a growing intensity of Al_4Pt lines, with ϵ-metastable phase tending to disappear. After further annealing for 150 h, ϵ lines were hardly visible.

2.3. ϵ-metastable phase

In the examined range of Pt concentrations (up to 3 at.%), two phases could be distinguished in both quenched and annealed samples. One of them (Fig. 2b) could be indexed on the basis of the previously reported structures of the Al_4Pt phase, taking the cubic cell $a = 19.23$ Å [8] or pseudotetragonal $a = 19.0$ Å and $c = 10.8$ Å [9]. The other, which proved to be metastable (we called it ϵ-metastable), could not be identified with any familiar intermediate phase in the Al-Pt system [8-10]. Forty diffraction lines belonging to this unknown phase were observed and after several trial-and-error procedures, the best indexing was obtained with a tetragonal cell with parameters $a = 13.58_0$ Å and $c = 16.64_6$ Å. Calculated and measured d_{hkl} values are given in Table II.

TABLE II Observed and calculated d_{hkl} values of the ϵ-metastable phase. Structure: tetragonal; lattice parameters: $a = 13.58_0$ Å, $c = 16.64_6$ Å, $c/a = 1.23$.

hkl	d_{calc} (Å)	d_{obs} (Å)
100	13.580	13.522
101	10.523	10.500
111	8.318	8.270
002	8.323	
200	6.790	6.841
210	6.073	6.074
003	5.548	5.533
202	5.261	5.259
212	4.906	4.907
004	4.162	4.160
222	4.159	
302	3.977	3.935
114	3.819	3.819
320	3.767	3.768
223	3.630	3.642
303	3.508	3.510
322	3.431	3.433
214	3.434	
313	3.397	3.397
410	3.294	3.274
105	3.235	3.232
330	3.201	3.209
224	3.145	3.145
420	3.037	3.040
403	2.897	2.901
422	2.853	2.855
006	2.775	2.775
500	2.717	2.720
305	2.682	2.683
511	2.630	2.621
424	2.453	2.452
600	2.264	2.262
620	2.147	2.147
533	2.148	
406	2.148	
336	2.096	2.096
426	2.048	2.048
632	1.967	1.964
506	1.941	1.939
545	1.789	1.791
408	1.774	1.779
800	1.697	1.697
705	1.676	1.677
716	1.579	1.579
806	1.448	1.449

3. Discussion

With regard to X-ray examination, the numerous new metastable intermediate phases obtained by the use of liquisol-quenching have the main disadvantage that they are produced in polycrystalline form. Failure to obtain single crystals often makes an accurate structure determination impossible. However, in certain cases, particularly when a new phase has a tetragonal unit cell, it is possible with some speculative calculations to obtain further information about the structure [11-13].

The lattice parameter of the ϵ-metastable phase can be related to the fcc α-Al as

$$a_{\text{tet}} \simeq \sqrt{45}\,\frac{a_\alpha}{2} \text{ and } c_{\text{tet}} \simeq 4a_\alpha .$$

The tetragonal unit cell of ϵ-phase can be built of forty-five α-Al fcc unit cells and may contain 180 atoms per unit cell if we assume the same packing as in the fcc structure. This suggestion gains support from the mean atomic volume of the ϵ-phase, calculated on the basis of 180 atoms per unit cell. The obtained value of 17.05 $Å^3$ is almost identical with the atomic volume of

Al_4Pt which is 17.09 Å^3, calculated on the basis of 416 atoms per unit cell [8]. The assumption that each unit cell contains 180 atoms led us to the chemical composition Al_5Pt for ϵ-metastable phase, i.e. thirty formula units per unit cell.

The appearance of ϵ-phase in annealed α-Al samples led us to the conclusion that ϵ-metastable is not formed directly on liquisol-quenching but only subsequently. The presence of ϵ-metastable in as-quenched samples can be explained on the basis of the decomposition process of α-Al during quenching. In samples which were not quenched fast enough to produce or to retain all Pt atoms in the solution, ϵ-metastable could be detected (samples thicker than 10 μm). The slower the quench (thicker samples), the higher the proportion of the Al_4Pt phase (Table I), which indicated that ϵ had begun to transform to Al_4Pt already in the quenching process. This is in agreement with the finding of Ruhl [14] and Dixmier and Guinier [15] that thinner samples are more effectively quenched. In water-quenched alloy, ϵ-metastable phase was completely absent.

Taking into account the results of X-ray diffraction we obtained with as-quenched and annealed samples we may say that the possible decomposition sequence for Al-rich Al-Pt solid solution is

$$\alpha\text{-Al} \rightarrow \epsilon\text{-metastable} \rightarrow \epsilon\text{-metastable} + Al_4Pt \rightarrow Al_4Pt\,.$$

However, the question still remains open whether the first step really exists, because in none of the as-quenched or annealed samples did we actually find ϵ-metastable phase without the presence of Al_4Pt.

4. Conclusions

1. With the aid of liquisol-quenching, metastable supersaturated Al-Pt solid solutions of up to 2.2 at. % Pt were found.

2. A new metastable phase was detected in as-quenched and annealed samples. This phase, denoted ϵ-metastable, could be indexed on the basis of the tetragonal cell with $a = 13.58_0$ Å and $c = 16.64_6$ Å, with 180 atoms per unit cell.

3. The chemical composition Al_5Pt was proposed for the new metastable phase.

4. The possible decomposition sequence for an Al-rich Al-Pt solid solution is

$$\alpha\text{-Al} \rightarrow Al_5Pt \rightarrow Al_5Pt + Al_4Pt \rightarrow Al_4Pt\,.$$

Acknowledgement

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