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# The effects of Ta additions on the phase compositions and high temperature properties of Pt base alloys

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#### Abstract

Pt–Al alloys attain high creep strength by precipitation hardening of the face-centred cubic matrix phase by the L1<sub>2</sub> ordered intermetallic  $\gamma'$  phase Pt<sub>3</sub>Al (analogous to Ni base superalloys). Along with superior environmental resistance these alloys have a potential as high-temperature materials. In this investigation the effect of Ta on strength, phase composition, lattice misfit and  $\gamma'$  volume fraction are assessed. Starting from the composition with 12 at.% Al, 5 at.% Cr and Pt balance, precipitation hardened Pt–Al–Cr–Ta alloys were analysed. Ta contents higher than 9 at.% lead to a decrease of  $\gamma'$  volume fraction. Ta increases the lattice parameters of both phases, but decreases the lattice misfit. By substitution of Al by Ta more Al partitions to the  $\gamma'$  phase, while Ta shows an inverse tendency. © 2007 Elsevier B.V. All rights reserved.

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### 1. Introduction

At present Ni base superalloys are the most advanced alloys for use in high-temperature applications up to about 1100 °C. These alloys exhibit the best combination of high-temperature mechanical properties and corrosion resistance in comparison with other materials. These two-phase alloys consist of a matrix or  $\gamma$  phase (Ni solid solution) and a  $\gamma'$  phase (L1<sub>2</sub> ordered with a composition close to Ni<sub>3</sub>Al). They contain up to 10 alloying additions and  $\gamma'$  volume fractions of up to 70% [1]. At this volume fraction the highest creep strength is observed [2]. However, the application of Ni base superalloys is limited by the melting point of Ni at 1455 °C. Considerably higher service temperatures require the development of materials based on elements with higher melting points.

One of the promising base elements is Pt due to its high melting temperature of 1770 °C. Alloys with Pt as base element are used for example in bushings for glass fibre fabrication [3]. In the glass industry, Pt alloys are generally used for their out-

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standing corrosion and oxidation resistance combined with good mechanical strength at ultra-high temperatures.

Precipitation hardened Pt base superalloys are analogous to the Ni base superalloys [4–9] in terms of a face-centred cubic (fcc) matrix strengthened by coherent precipitations of L1<sub>2</sub> ordered  $\gamma'$  particles. In Pt base superalloys the  $\gamma'$  phase has a composition close to Pt<sub>3</sub>Al. The microstructure of Ni base superalloys is regarded as a model for the development of Pt base superalloys.

In order to achieve high creep strength the following parameters have to be considered: size, form and arrangement of  $\gamma'$  particles, high  $\gamma'$  volume fraction, slow coarsening of the precipitates and optimised misfit between matrix and  $\gamma'$  particles.

Precipitation strengthened alloys of the system Pt–Al–Cr–Ni was studied in previous work [6–10]. The effects of Al, Cr and Ni additions and various heat treatments on the properties of Pt–Al–Cr–Ni alloys have been described in detail. Vorberg et al. [9] analysed the microstructure of Pt alloys by means of transmission electron microscopy (TEM). The authors observed  $\gamma'$  precipitates of irregular, cubical and round shape. Dislocation networks at the  $\gamma/\gamma'$  interface in some samples were visible. The shape of  $\gamma'$  particles and the dislocations structures in the investigated alloys are correlated with the misfit stresses.

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In the present work Pt alloys with the alloying elements Al, Ta and Cr are examined. Particularly the influence of Ta on the above-mentioned parameters was analysed. For microstructure analysis, scanning electron microscopy (SEM) was applied. Similar shapes of  $\gamma'$  precipitations as in TEM observations were detected, which again, can be related to misfit values.

In all examined alloys Al serves as  $\gamma'$  forming element. Numerous X-ray diffraction (XRD) experiments on ternary Pt–Al–X alloys from Hill et al. [4,5] have proven, that Cr stabilises the L1<sub>2</sub> structure of the  $\gamma'$  phase down to room temperature, moreover it has a positive effect on the high-temperature strength and phase stability. In this investigation, Al is substituted gradually by Ta.

#### 2. Experimental

Compositions of  $Pt_{83}Al_{12-x}Ta_xCr_5$  (with *x* changing from 0 to 12 with a step size of 3) were selected. All subscripts denote the composition of the corresponding element in at.%. Arc melted buttons were manufactured from pure elemental constituents of at least 99.9% purity under argon atmosphere and remelted five times in order to achieve homogeneity. Afterwards the buttons were heat treated at 1500 °C for 12 h and 1520 °C for 12 h in air in order to homogenize dendritic segregation. Since Al tends to evaporate during melting and it is also lost to the oxide scale, the actual compositions (Table 1) were determined by energy dispersive X-ray analysis (EDX) in the scanning electron microscope (SEM). Alloy names have been designated from Ta0 up to Ta12 according to their nominal Ta content in at.% (Table 1).

The homogenised alloys were further heat treated at 1100, 1200 or 1300 °C for 24 h in air followed by water quenching in order to freeze-in the high-temperature microstructure. Samples were ground, polished and electrolytically etched in an aqueous KCN solution for microstructure investigations. Compositions of coarse  $\gamma$  and  $\gamma'$  phases were determined by EDX. The  $\gamma'$  volume fraction was calculated from SEM micrographs using image analysis.

X-ray diffraction (XRD) was carried out with a Seifert 3000P diffractometer on polished surfaces of samples heat treated at 1200 °C. The goniometer was set up in Bragg–Brentano geometry with a primary SiO<sub>2</sub> monochromator placed in the diffracted beam in order to select the Cu K $\alpha_1$  wavelength only. XRD patterns were recorded with  $2\theta$  ranging from 20° to 90° with a scan step of 0.02°.

Table 1

Actual compositions of the alloys after solution heat treatment for 12 h at 1500  $^\circ C$  and 12 h at 1520  $^\circ C$ 

Nominal composition	Designation	Measured actual compositions				
		Pt	Al	Та	Cr	
Pt <sub>83</sub> Al <sub>12</sub> Cr <sub>5</sub>	Ta0	84.2	10.7	_	5.1	
Pt83Al9Ta3Cr5	Ta3	84.0	8.3	2.9	4.8	
Pt83Al6Ta6Cr5	Ta6	83.6	5.7	6.1	4.6	
Pt83Al3Ta9Cr5	Ta9	83.2	2.9	9.3	4.6	
Pt <sub>83</sub> Ta <sub>12</sub> Cr <sub>5</sub>	Ta12	82.6	-	11.8	5.6	

Experimental XRD patterns were low pass filtered in order to reduce noise. By means of the software *PowderCell* [11] a diagram of the binary Pt–Al system was simulated assuming L1<sub>2</sub> structure for Pt<sub>3</sub>Al and fcc structure for Pt. *PowderCell* calculates entire XRD patterns using overlapping Pseudo-Voigt functions for individual XRD peaks. The phase lattice parameters were taken from [12,13] for pure platinum and from [14,17] for the L1<sub>2</sub> structure of the Pt<sub>3</sub>Al  $\gamma'$  phase.

The experimental diagram of each alloy was compared with the simulated diagram for qualitative phase identification. Lattice parameters  $a_{\gamma}$  and  $a_{\gamma'}$  were determined by the use of Bragg's equation. Using all visible peaks, the  $\gamma/\gamma'$  lattice misfit  $\delta = 2(a_{\gamma'} - a_{\gamma})/a_{\gamma'} + a_{\gamma}$  was calculated.

Cylindrical samples (3 mm height and 2.7 mm diameter) were cut from homogenised button ingots. With these samples slow compression tests at 1000 and 1200 °C were performed with a compression rate of  $10^{-5}$ /s. The maximum stress was determined from compression stress–strain diagrams. The microstructures have been analysed using secondary electron (SE) images recorded with a ZEISS 1540 EsB field emission scanning electron microscope (SEM).

#### 3. Results

#### 3.1. Microstructure after homogenisation $(1520 \,^{\circ}C)$

Fig. 1 shows the microstructures of the five alloys after annealing for 12 h at 1500 °C and 12 h at 1520 °C subsequently water quenched. Three of the five alloys exhibit a two-phase microstructure. The  $\gamma'$  phase with a composition close to Pt<sub>3</sub>(Al, Ta, Cr) is dark shaded, while the bright phase is the Pt rich solid solution matrix. In the ternary alloy Ta0 the distribution of the precipitates is monodispers throughout the sample with only one particle size distribution, with an edge length of 50–100 nm (Fig. 1a). In alloy Ta3 alternate monodispers and bidispers regions can be seen (Fig. 1b). In the system Ta6 a bidispers distribution is observed (Fig. 1c). The remaining two alloys Ta9 and Ta12 are  $\gamma'$  free, resulting in a single-phase matrix material (Fig. 1d and e).

Relatively large and irregular shaped  $\gamma'$  particles indicate, that at 1520 °C the material could not be completely homogenised in the single-phase  $\gamma$  region. The fine and uniformly distributed precipitates are formed during quenching of the sample.

The influence of cooling rate on the alloy microstructure was checked. For this purpose a self-made device for quenching in liquid Ga under vacuum was developed. In Fig. 2a and b the microstructure of the alloy Ta3 after the homogenisation and quenching in water is shown. In addition to relatively large  $\gamma'$  areas, very fine precipitations of 50–150 nm in size are observed.

Fig. 2c and d show the sample of Fig. 2a and b after an additional heat treatment for 30 min at 1520 °C in order to resolve fine  $\gamma'$  particles. The specimen was quenched very rapidly in liquid Ga.

In Fig. 2c and d only relatively coarse  $\gamma'$  particles with 1–5  $\mu$ m in size are observed. With the much higher cooling rate achieved by quenching in liquid Ga, there are no small

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