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Synthesis and characterization of a new modification of PtAl

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A new PtAl phase, which is stable at room temperature under oxidizing conditions, has been synthesized at 200 °C and 5 MPa. X-ray studies reveal it to be different from the known polymorphs of PtAl, which crystallize in the FeSi and CsCl structure types. The crystal structure of the new PtAl modification is found to be isotypical with the low-temperature modification of PdAl. *In situ* high-temperature X-ray diffraction experiments in air were performed to study the thermal behavior of the new PtAl alloy. In the temperature range between 400 and 700 °C, Pt_5Al_3 forms as an intermediate phase. At higher temperature the alloy decomposes, resulting in the formation of platinum and Al_2O_3. The thermodynamic instability at high temperatures explains why this new modification has not been observed using contemporary metallurgic processes. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: Pt-Al phase; synthesis; X-ray

INTRODUCTION

Intermetallic phases of aluminum with transition metals or noble metals, such as platinum or rhodium, the so called aluminides, are desirable materials due to their extraordinary physical properties. The materials are usually extremely stable under high-temperature treatment and are resistant to attack by oxygen. Particularly useful is the low density of the materials compared with the transition metal or noble metal. Owing to their high resistance to environmental influences, aluminides are used as coating material, e.g. for gas turbine blades or car engines.[1–3]

The phase diagram of the binary Pt–Al system and the intermetallic phases formed have been studied and discussed extensively in the literature.[4–11] Some of the stable phases, such as PtAl, Pt_3Al, Pt_5Al_3, Pt_2Al_3, $PtAl_2$, Pt_8Al_{21}, and Pt_5Al_{21}, are also known to form polymorphs.

Hitherto, two different crystallographic forms of PtAl have been reported in the literature. A low-temperature form of PtAl crystallizes in the FeSi structure type and has been described by Ferro *et al.*[12] Bhan and Kudielka[5] describe the synthesis of PtAl by melting aluminium and platinum under an argon atmosphere. High-temperature X-ray experiments between 1000 and 1200 °C show the coexistence of two phases. The phase Pt_5Al_3 occurs together with a PtAl phase (FeSi structure type). In the temperature range between 1270 to 1340 °C, Bhan and Kudielka[5] observed a high-temperature form of PtAl with the CsCl structure type.

Recently, we were able to synthesize a very fine β-NiAl powder from the organometallic compounds $[(cod)_2Ni]$ (cod = cycloocta-1,5-dien) and $Al(ethyl)_3$.[13,14] An application of this synthesis concept to other systems resulted in the synthesis of Pt–Al alloys. In this work, we describe the synthesis and characterization of a new modification of PtAl by this method. This route has the potential to open pathways for the synthesis of new phases and new polymorphs for intermetallic compounds.

EXPERIMENTAL

Synthesis of the material[15]

1.59 g (3.86 mmol) of the starting material, $[(cod)]_2Pt$, was dissolved in 100 ml of toluene at room temperature (RT), giving a clear yellow solution. Then, 0.53 ml (0.44 g, 3.86 mmol) of $Al(ethyl)_3$ was added and the mixture was stirred for 24 h at RT. The reaction of $[(cod)]_2Pt$ with $Al(ethyl)_3$ resulted in the formation of a clear dispersion with a gray–black color. After the removal of the solvent and the subsequent drying process under vacuum

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conditions (10^{-2} Pa), an air-sensitive solid was isolated. The hydrogenation of this solid at 200 °C and a pressure of about 5 MPa resulted in the formation of the highly dispersed PtAl powder. Chemical analysis shows the product to have the following composition (wt%): Pt, 85.7; Al, 12.9; C, 0.73; H, 0.18; yield: 0.849 g (99.1% of theory). Theoretical composition (wt%): Pt, 87.8; Al, 12.2.

Thermal analyses

The differential scanning calorimetry (DSC) data were collected with a Netzsch STA 449c. The samples were placed into alumina crucibles and heated in air at a rate of 10 °C min^{-1} from RT up to 950 °C.

X-ray characterization

A number of different X-ray diffraction experiments were used to characterize the synthesized PtAl sample. To avoid absorption effects, the chemically synthesized sample ($PtAl_{\text{as made}}$) was analyzed at RT using a Stoe STADI P $\theta - \theta$ diffractometer in reflection geometry with a secondary monochromator and a scintillation counter.

For the characterization of the intermediate phase formed at elevated temperatures, a small amount of the fresh sample was calcined for 4 h in an oven at 550 °C and subsequently cooled to RT ($PtAl_{550}$). The sample was filled into a glass capillary (0.5 mm outer diameter) and measured at RT on a Stoe STADI P diffractometer in transmission geometry (Debye–Scherrer geometry), which enables small sample amounts to be analyzed. The diffractometer was equipped with a primary monochromator and a linear position-sensitive detector enabling the simultaneous data acquisition in the 2θ range of 6°.

The X-ray analysis of the sample calcined at 1350 °C ($PtAl_{1350}$) was also performed on the Stoe STADI P transmission diffractometer equipped with the position-sensitive detector. For the *in situ* high-temperature experiments, a graphite oven mounted on the transmission diffractometer was used. A curved position-sensitive detector, which covered a 2θ range of approximately 40° enabled the reduction of data acquisition times. For the measurements, the sample was introduced into a quartz glass capillary and measured in air. The sample was heated from RT up to 900 °C in temperature steps of 25 °C and a heating rate of 10 °C min^{-1}. The measurement conditions are given in Table 1.

Transmission electron microscopy

The chemically synthesized $PtAl_{\text{as made}}$ sample was also investigated by means of transmission electron microscopy (TEM) using a Hitachi HF2000 transmission electron microscope equipped with a cold field emitter gun. A Noran Voyager energy dispersive X-ray (EDX) system with Si(Li)-detector was used for elemental analysis on the nano-scale.

Image acquisition and image processing were performed using a KeenView CCD camera with analysis software, both from Soft Image Systems. The PtAl powder was supported on a lacey carbon–copper grid as a dry powder. The exposure time of the CCD camera ranged typically between 0.5 and 2 s. The spot size for EDX measurements was about 5–8 nm, with an acquisition time (lifetime) of 60–120 s for each measurement.

RESULTS AND DISCUSSION

Identification and a preliminary characterization of the sample synthesized were undertaken using a data set collected on a Bragg–Brentano diffractometer at RT. The reflections of the powder diagram shown in Fig. 1a cannot be assigned to any known PtAl phase in the PDF-2 database. The database contains 11 entries for PtAl phases, but there exists no entry for a PtAl alloy with the composition Pt:Al =1 : 1.

Several different intermetallic PtAl phases are described in the literature; some include the crystal structure data. The low-temperature form of PtAl crystallizes in the FeSi structure type and has been described by Ferro *et al.*[12] Bhan and Kudielka's[5] high-temperature form of PtAl analyzed at temperatures above 1200 °C crystallizes in the CsCl structure

Table 1. Sample assignment, sample treatment, and measurement conditions used for the X-ray diffraction experiments

Sample assignment	Sample treatment	Temperature during measurement	Diffractometer	Wavelength	2θ range°	2θ step size°	Counting time/step (s)
$PtAl_{\text{as made}}$	Sample as made	RT	Stoe STADI P $\theta - \theta$	Cu $K_{\alpha 1,2}$	5–100	0.04	25
$PtAl_{550}$	Heated to 550 °C, cooled to RT	RT	Stoe STADI P transmission diffractometer	Cu $K_{\alpha 1}$	10–60	0.01	12 000
$PtAl_{1350}$	Heated to 1350 °C, cooled to RT	RT	Stoe STADI P transmission diffractometer	Cu $K_{\alpha 1}$	10–90	0.01	12 000
$PtAl_{in\ situ}$		RT–900 °C	Stoe STADI P transmission diffractometer	Cu $K_{\alpha 1}$	20–60	0.01	3600

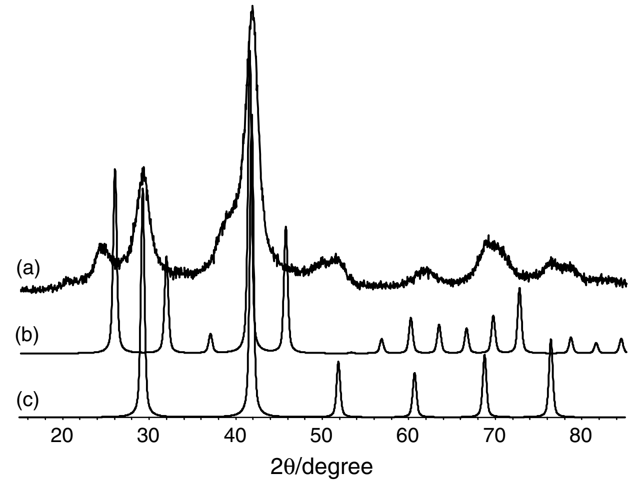

Figure 1. (a) Powder pattern of the chemically synthesized $\mathrm{PtAl_{as\ made}}$ sample measured at RT; (b) simulated powder pattern for the PtAl polymorph in the FeSi structure type; (c) simulated powder pattern for the PtAl polymorph in the CsCl structure type.

type. The crystallographic data of both modifications were used for the simulations shown in Fig. 1b and c, and are shown with the measured powder diagram of the sample (Fig. 1a).

A comparison of the observed and simulated patterns in Fig. 1 shows clearly that the measured reflections of the sample match neither the simulated pattern for PtAl with the FeSi structure type (Fig. 1b) nor that of the CsCl structure type (Fig. 1c). Also, comparison with powder patterns of other intermetallic phases described in the literature showed no exact matches.

Unfortunately, the reflections observed are very broad, which can be attributed to small particle sizes of the crystals confirmed by TEM investigations. As a result, the exact determination of the space group and the lattice parameters is problematic. However, the search was extended to other systems, and a good match was achieved with the powder diagram of PdAl (PdAl structure type) described by Matkovic and Schubert.[16] This phase is stable below 840 °C and crystallizes in the space group $R\overline{3}$. Two high-temperature structures are known for PdAl. One phase is stable above 1045 °C and crystallizes in the CsCl type,[17] and a second one, stable between 700 and 1040 °C, is assigned to the FeSi structure type.[17,18]

The crystal structure data of PdAl[16] were used as starting parameters for a Rietveld refinement and the palladium atoms were substituted by platinum atoms. Owing to the poor resolution of the data, caused by small particles, the refinement could only be performed by using constraints on the interatomic distances and angles. Since the fully constrained refinement does not reveal any additional information about the structure of PtAl, apart from the fact that it is isostructural with hexagonal PdAl, we report here only the lattice constants obtained by the refinement. The refined lattice constants of the new PtAl modification are $a = 15.605(6)$ Å and $c = 5.276(3)$ Å. A plot showing the measured and the calculated patterns is given in Fig. 2.

Investigation of the thermal properties of this new PtAl phase was performed by *in situ* high-temperature X-ray experiments in order to observe possible phase transformation processes. The corresponding powder patterns (Fig. 3) reveal the appearance of new reflections, besides the reflections belonging to PtAl at 23, 29, 33, 40, and 45° 2θ at about 400 °C. The intensities of the reflections become weaker at temperatures above 750 °C, and above 800 °C only reflections belonging to pure platinum are observed.

In order to study whether the phase observed during the *in situ* X-ray experiments in the temperature range between 400 and 700 °C is metastable or not, *ex situ* X-ray experiments were

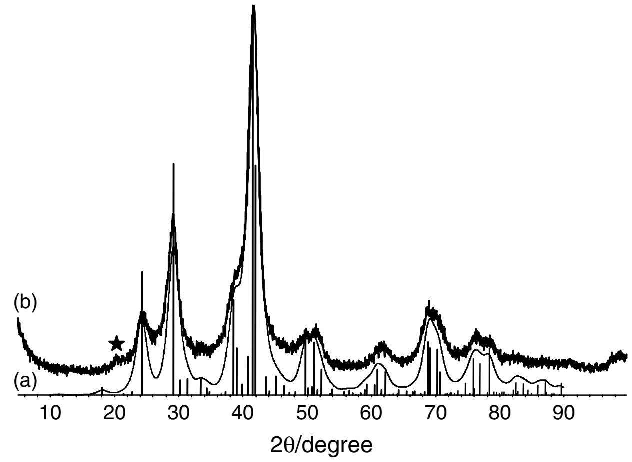

Figure 2. (a) Measured powder pattern of the synthesized $\mathrm{PtAl_{as\ made}}$ sample and (b) simulation of the powder pattern using PdAl structure type and the refined lattice constants for PtAl. The positions of the single reflections are marked by the vertical lines. The reflection labeled ⋆ is assigned to an impurity.

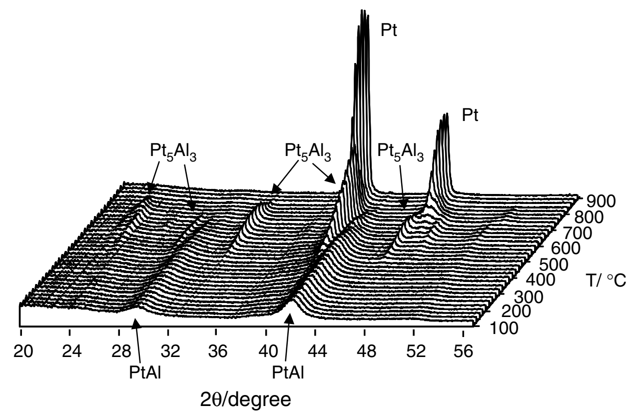

Figure 3. Powder patterns collected *in situ* in the temperature range between 100 and 900 °C.

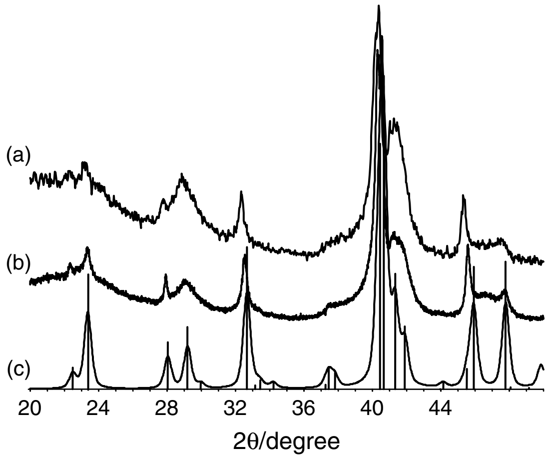

Figure 4. Powder patterns of: (a) PtAl measured *in situ* at 550 °C ($PtAl_{in\ situ}$); (b) PtAl measured at RT after heating to 550 °C and subsequent cooling ($PtAl_{550}$); (c) simulation of the powder diagram of Pt_5Al_3. The theoretical reflection positions are marked by the vertical bars.

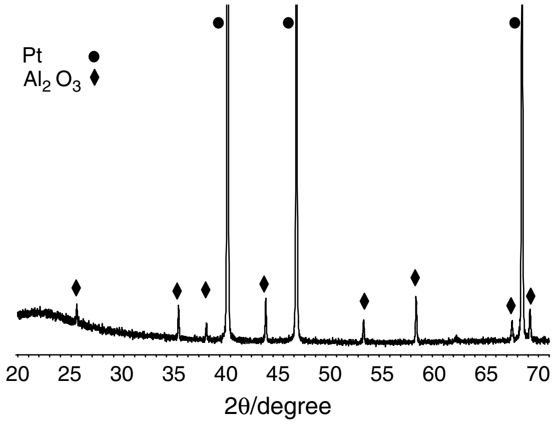

Figure 5. Powder pattern of the sample after calcination at 1350 °C for 12 h ($PtAl_{1350}$). Sample measured at RT. The reflections of corundum and platinum are marked by symbols.

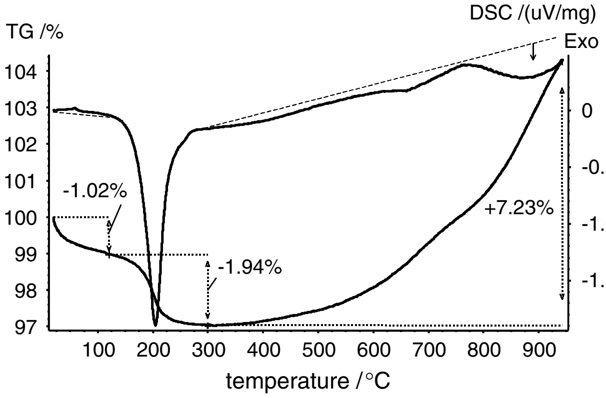

Figure 6. DSC curve of PtAl collected between RT and 900 °C in air.

performed. Figure 4 compares the powder pattern collected *in situ* at 550 °C ($PtAl_{in\ situ}$) with the pattern of the sample collected *ex situ* at RT after the temperature treatment at 550 °C ($PtAl_{550}$). This shows that the phase formed above 400 °C is also stable at RT. Simulation of the powder pattern of Pt_5Al_3 using the crystal structure data of Bronger and Wrzesien[19] reveals a good agreement. Bhan and Kudielka[5] and Chattopadhyay and Schubert[6] describe the coexistence of Pt_5Al_3 and PtAl and a phase separation process during quenching.

A further increase of the temperature leads to the formation of crystalline platinum, as the *in situ* studies show. During the temperature treatment, a decomposition of the alloy takes place: platinum crystallizes. Interestingly, crystalline aluminum was not observed. To prove the presence of elemental aluminum, the sample was heated to 1350 °C and kept for 12 h at that temperature before it was cooled to RT ($PtAl_{1350}$). X-ray analysis shows corundum (Al_2O_3) reflections and the platinum reflections (Fig. 5), proving the presence of aluminum after the decomposition of the alloy. Thus, the successive temperature increase from RT to 1350 °C induces a phase separation via the transformation of the starting material to Pt_5Al_3. Platinum and aluminum oxide are formed at high temperatures in air under normal pressure conditions.

A DSC curve of the new phase displays a slightly endothermic reaction below 150 °C, followed by an exothermic reaction with a maximum at about 200 °C (Fig. 6). These can be attributed to the desorption of physisorbed molecules and the combustion of residual organics on the surface of the material. The total weight loss up to 300 °C is about 3 wt%. At temperatures above 350 °C an increase of the weight of the sample is observed, which is caused by successive exothermic processes. The increase in weight is most likely due to the formation of aluminum oxide from the aluminum formed during the decomposition of the alloy. As expected, the oxidation of aluminum is enhanced at temperatures above 600 °C, where X-ray studies showed the decomposition of the Pt_5Al_3 intermediate to take place.

The TEM micrograph of the freshly synthesized PtAl sample prepared on a lacey carbon grid (Fig. 7a) shows a homogeneous conglomerate of individual nano-crystalline particles. The sizes of the individual particles range from 5 to 10 nm. They are embedded in a thin matrix of residual hydrocarbons. EDX spot analysis yielded a homogeneous distribution of aluminum and platinum with an atomic ratio of about 1 : 1. No nano-particles composed of pure aluminum or platinum were observed. The high-resolution micrograph (Fig. 7b) reveals that the single crystallites have random orientation.

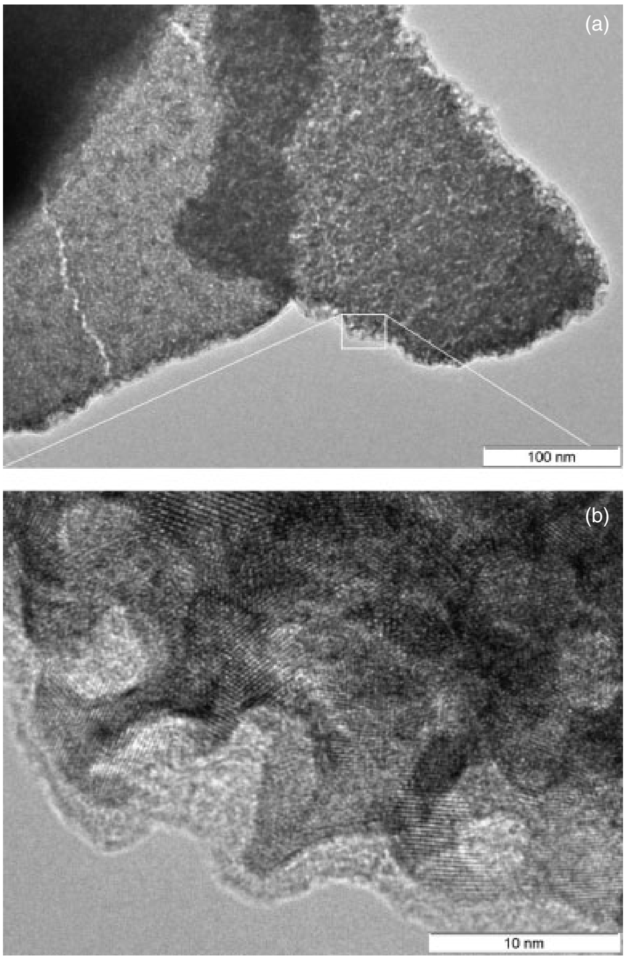

Figure 7. TEM micrographs of the $PtAl_{as\ made}$ sample: (a) overview, showing the homogeneous conglomerate of the nano-sized particles; (b) high-resolution TEM image of the randomly orientated crystallites.

CONCLUSION

X-ray studies reveal a new crystallographic modification of PtAl in the binary Pt–Al system. The new PtAl phase, which is stable at RT under oxidizing conditions, was synthesized at 200 °C and 5 MPa. Hitherto, only PtAl phases with the FeSi or CsCl structure types have been reported in the literature. The crystal structure of the new PtAl modification crystallizes in the hexagonal PdAl structure type. A homogenous distribution of platinum and aluminum without the formation of nano-particles consisting of the pure metals is confirmed by TEM studies.

In situ high-temperature X-ray diffraction experiments of the PtAl sample show the formation of Pt_5Al_3 as an intermediate phase in the temperature range between 400 and 700 °C ($5PtAl \rightarrow Pt_5Al_3 + 2Al$). At higher temperatures the Pt_5Al_3 alloy decomposes ($Pt_5Al_3 \rightarrow 5Pt + 3Al$), a phase separation takes place, and the crystallization of platinum and Al_2O_3 is observed. The latter is formed by the oxidation of aluminum released first by the transformation of the PtAl into Pt_5Al_3 and then by the decomposition of that intermediate phase into platinum and aluminum.

The thermodynamic instability at high temperatures explains why this new modification has not been formed during contemporary metallurgic processes, which take place at temperatures above the decomposition temperature of the new phase.

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