

New intermetallic compounds in the Ce–Pt system

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Abstract The Ce-rich part of Ce–Pt phase diagram has been investigated by means of differential thermal analysis (DTA), X-ray diffraction (XRD), optical and electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Two new intermediate phases, Ce_5Pt_3 and Ce_5Pt_4 , have been discovered and found to crystallize with tetragonal Pu_5Pd_3 -type structure and orthorhombic Ge_4Sm_5 -type structure, respectively. All the Ce-rich compounds of the system were found to crystallize with a peritectic type formation. We have determined the temperatures of the peritectic plateaus and established the liquidus curves up to 1500 °C.

Keywords Rare-earth intermetallics · Phase identification · Differential thermal analysis · X-ray diffraction · Metallographic techniques

Introduction

We have demonstrated the potential of the method consisting in the oxidation of gold alloys to produce highly loaded gold catalysts [1, 2]. More recently, we have patented a new process of elaboration of Pt-based catalysts by low-temperature oxidation of Ce–Pt intermetallic precursors [3]. The use of our process would yield high-loaded Pt

catalysts. The control over the nanocomposite properties (size and morphology of the particles) requires the knowledge of the microstructure and of the phases present in the metallic precursors; so the binary phase diagram of the Ce–Pt system is needed.

In the assessed version of the diagram proposed by Massalski et al. [4], based on crystallographic data [5–10] and phase equilibria encountered in the homologous Nd–Pt system [11], a phase diagram has been proposed containing two Ce-rich, three Pt-rich and the equiatomic compounds. However, the liquidus curves have not been clearly established and the stability of the reported compounds is still speculative. In this article, we present a new version of phase equilibria in a composition range from 30 to 50 at.% Pt where two new phases have been evidenced.

Experimental procedures

The samples were prepared by arc-melting under an argon atmosphere from Ce ingots and Pt wires with 99.9% and 99.95% purity, respectively. Residual oxygen was removed from the furnace by melting pure cerium prior to alloy synthesis. In order to ensure a homogeneous composition of the ingot, the alloys were re-melted at least three times. The weight loss did not exceed 0.5%. As the vapour pressure values for Pt and Ce are low and similar— 1.1×10^{-6} and 7.2×10^{-5} atm, respectively at 1900 °C [12]—the resulting uncertainty over the alloy composition does not affect the conclusions drawn from our experimental results. In order to reach the equilibrium state, the samples were annealed at different temperatures from 400 to 1050 °C with a duration up to 11 months. They were wrapped in tantalum foils and sealed under argon in quartz tubes. Titanium foils were used as oxygen getter.

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The DTA measurements were carried out with a SETARAM TGA92 apparatus using a DSC cell and under an argon atmosphere up to 1550 °C. The samples were placed in tungsten crucibles applying heating rates of 5 and 10 °C/min. The temperatures of the phase transitions were determined with an accuracy of 5 °C. Because of low kinetics of the peritectic reaction, the equilibrium state cannot be reached during analysis on cooling. Thus, only thermal events detected on heating on equilibrated samples were taken into account for the establishment of the phase diagram. The mass of the samples were systematically monitored by thermogravimetry during experiments; no weight change that could be due to a reaction with residual oxygen was detected.

Metallographic examinations were performed by means of optical and scanning electron microscopy (JEOL 6400). The quantitative analysis of elements in individual phases was done by EDX with an uncertainty of ± 1 at.% using Ce- L_{α} (4.287 keV) and Pt- L_{α} (9.441 keV) radiations with an acceleration voltage of 20 keV.

X-ray diffraction patterns were collected using a position sensitive detector (INEL-CPS 120, Co- K_{α} , $10 \leq 2\theta \leq 120^\circ$). Experiments were performed under vacuum to avoid oxidation of the powders adding Si powder as an internal standard. The determination of the crystal structure of Ce_5Pt_4 was done on single crystal using an Enraf-Nonius CAD 4 automatic 4-circle diffractometer with graphite-monochromated Mo- K_{α} radiation.

The main difficulty encountered during this study was the extremely rapid oxidation of the alloys. This is why all operations were carried out under vacuum or inert atmosphere.

Results and discussion

Phase equilibria

Two new intermediate phases, Ce_5Pt_3 and Ce_5Pt_4 , have been evidenced in the Ce-rich part of the Ce–Pt system. The presence of these peritectic compounds changes the phase equilibria previously assessed [4].

We confirmed that the compound Ce_7Pt_3 discovered by Olcese [5] is formed by a peritectic reaction. We measured the temperature of the formation at 861 ± 7 °C (Fig. 1) but we found that the compound is formed from the new phase Ce_5Pt_3 (37.5 at.% Pt). Several facts confirm this result: (i) we found a new peritectic plateau at 936 ± 8 °C (Fig. 1) which cannot be related neither to Ce_7Pt_3 nor Ce_3Pt_2 ; (ii) a Tammann analysis performed on the plateau at 861 °C (Fig. 2) shows that it ends at a composition about 37 at.% Pt where the endothermic effect of the new invariant is a maximum; (iii) metallographic observations

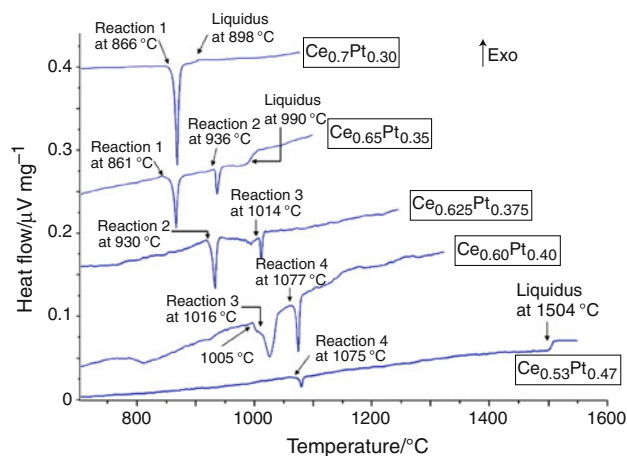


Fig. 1 DTA curves of Ce-rich Ce–Pt alloys. Reaction 1: liquid + $Ce_5Pt_3 \leftrightarrow Ce_7Pt_3$; reaction 2: liquid + $Ce_3Pt_2 \leftrightarrow Ce_5Pt_3$; reaction 3: liquid + $Ce_5Pt_4 \leftrightarrow Ce_3Pt_2$; reaction 4: liquid + $CePt \leftrightarrow Ce_5Pt_4$

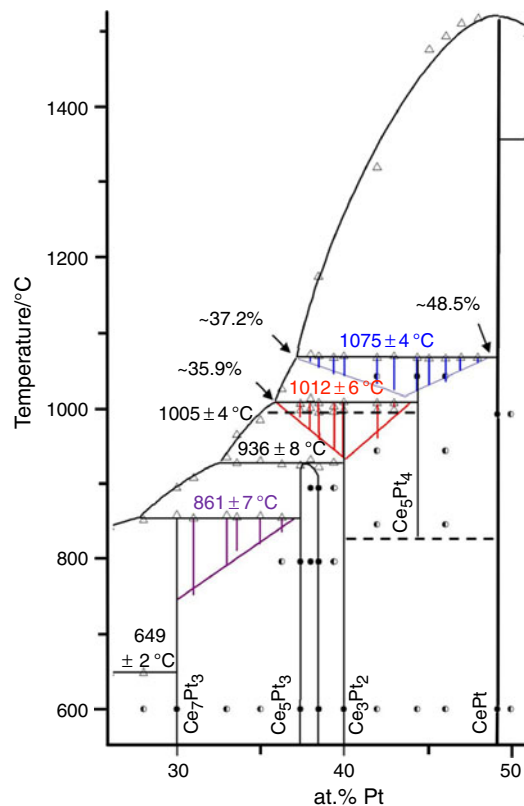


Fig. 2 Ce–Pt phase diagram from 30 to 50 at.% Pt. Triangle DTA; filled circle single-phase domain, half-filled circle two-phase domain. Tammann analyses have been applied on the plateaus detected at 861, 1012 and 1075 °C

revealed that a sample at 37.5 at.% Pt annealed at 600 °C for 4 months is single-phase and a sample at 39.2 at.% Pt annealed at 900 °C for 1 month contains two phases, Ce_5Pt_3 and Ce_3Pt_2 . Combining metallographic observations and XRD analysis, we propose a narrow homogeneity domain for Ce_5Pt_3 ranging from 37.5 to 38.5 at.% Pt.

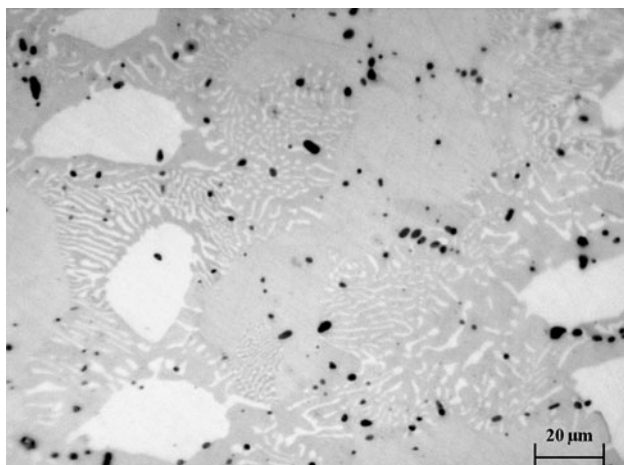


Fig. 3 Optical micrograph of a post-DTA sample with the composition of 44.4 at.% that reveals a lamellar eutectoid microstructure ($\text{Ce}_3\text{Pt}_2 + \text{CePt}$) obtained by the decomposition of Ce_5Pt_4 at low temperature

We also found that the peritectic formation of Ce_3Pt_2 implies another new compound, Ce_5Pt_4 , giving: liquid + $\text{Ce}_5\text{Pt}_4 \leftrightarrow \text{Ce}_3\text{Pt}_2$. We measured the temperature of the peritectic formation of Ce_3Pt_2 at 1012 ± 6 °C (Fig. 1). Another invariant detected by DTA at 1005 ± 4 °C was attributed to this compound because the endothermic effect is maximal at its composition and cannot be related to the neighbouring phases. The narrow temperature range (1005–1012 °C) between the two plateaus does not let us identify the origin of the transition occurring at 1005 °C. So, we suggest that Ce_3Pt_2 may undergo an allotropic transformation at 1005 °C.

Ce_5Pt_4 is formed by the peritectic reaction, liquid + $\text{CePt} \leftrightarrow \text{Ce}_5\text{Pt}_4$, which occurs at 1075 ± 4 °C (Fig. 1). The existence of Ce_5Pt_4 was confirmed by metallographic observations, EDX measurements and DTA. For instance, the Tammann analyses (Fig. 2) show that the plateau of the peritectic formation of Ce_3Pt_2 ends at 44 at.% Pt where the endothermic effect for the formation of Ce_5Pt_4 is maximal. We observed that Ce_5Pt_4 decomposes at low temperature. Indeed, the XRD and the metallographic observations of a sample at 44.4 at.% Pt annealed at 600 °C for 4 months reveal that it contains Ce_3Pt_2 and CePt . The disappearance of Ce_5Pt_4 at low temperature suggests the presence of an eutectoid-type decomposition. In order to confirm this assumption, we verified the microstructure of post-DTA samples around the composition of 44.4 at.% Pt. From Fig. 3, which illustrates an optical micrograph of a sample after DTA, one can see a characteristic lamellar microstructure, Ce_3Pt_2 (white phase) + CePt (dark-gray phase), confirming the eutectoid decomposition of Ce_5Pt_4 grains (light-gray phase). It is noteworthy that the reaction front has been stopped on cooling that shows the slow kinetics of a solid-state transformation. Thus, we understand why we

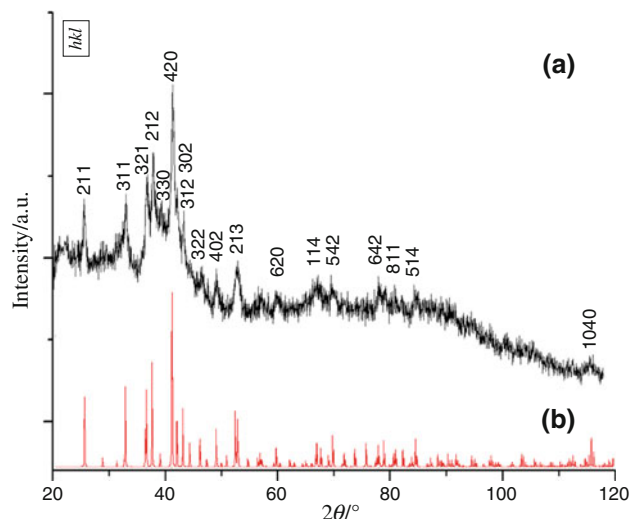


Fig. 4 X-ray powder diffraction pattern of Ce_5Pt_3 (a) compared with the calculated Pu_5Rh_3 -type pattern (b)

have not detected this decomposition by DTA in spite of the use of several heating rates (1, 2, 5, 10 °C/min). Taking into account for metallographic and XRD results, performed on samples with compositions close to 44.4 at.% Pt and annealed at different temperatures, we propose a temperature of the eutectoid reaction occurring between 600 and 850 °C.

Crystallographic investigation

Figure 4 shows the experimental powder XRD pattern of Ce_5Pt_3 which covers perfectly the calculated pattern for a tetragonal Pu_5Rh_3 -type structure already reported for the homologous compound Ce_5Ir_3 [13]. The lattice parameters were refined to $a = 11.405(7)$ Å and $c = 6.648(4)$ Å by means of CELREF software [14].

The single-crystal study of Ce_5Pt_4 gives the orthorhombic Ge_4Sm_5 -type structure with $a = 7.665$ Å, $b = 15.066$ Å and $c = 7.616$ Å. This structure type has already been reported for homologous compounds [13, 15–17], particularly for heavy rare-earth/platinum alloys.

Summary

The Ce-rich part of Ce–Pt phase diagram (Fig. 2) was investigated on the basis of DTA, XRD, EDX and metallographic studies. Two new compounds, Ce_5Pt_3 and Ce_5Pt_4 , have been discovered and their crystal structures have been identified. The temperatures and the types of formation of compounds already reported have been clarified taking into account for the existence of the new compounds. Moreover, the stability range of all compounds in the Ce-rich region has been determined. The liquidus

curves have been established as high as 1500 °C; thanks to DTA performed in W crucibles.

As far as applications are concerned, these results provide essential information for the synthesis of Pt-catalysts supported on simple or mixed oxides (i.e. ZrO₂, CeO₂). They also give experimental data needed for the calculation of phase diagrams; Ce–Pt and higher-order diagrams such as Ce–Zr–Pt.

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