ELSEVIER

Journal of Alloys and Compounds 239 (1996) 226–230

Journal of ALLOYS AND COMPOUNDS

A revision of the binary system Ag–Pt

Ph. Durussel, P. Feschotte*

Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH, CH-1015 Lausanne-Dorigny, Switzerland

Received 22 January 1996

Abstract

A complete revision of the binary system Ag–Pt by DTA, X-ray diffraction and EMPA on long-time annealed specimens confirms the peritectic formation of the solid solution of Ag at 1188 ± 3°C and 40 at.% Pt. However, only the intermediate stoichiometric phase $Ag_{47}Pt_{53}$ is found, corresponding to the formula $Ag_{15}Pt_{17}$ and having a complicated structure.

Keywords: Silver–platinum compounds; Ag–Pt phase diagram; DTA; XRD; EPMA

1. Introduction and previous work

The previously assessed Ag–Pt phase diagram [1] (Fig. 1) shows that little change has been proposed since Schneider and Esch [2] published a surprising ordering of the silver-rich solid solution as well as three intermediate compounds at 58, 65 and 85 at.% Pt, below 700°C. In order to clarify the possible solid transformation in the Ag–Pt alloys, we prepared 60 specimens of varying compositions. These alloys were annealed for much longer times (120 days at 750°C for example, instead of 30 days at 770°C [2]) in order to obtain equilibrium conditions.

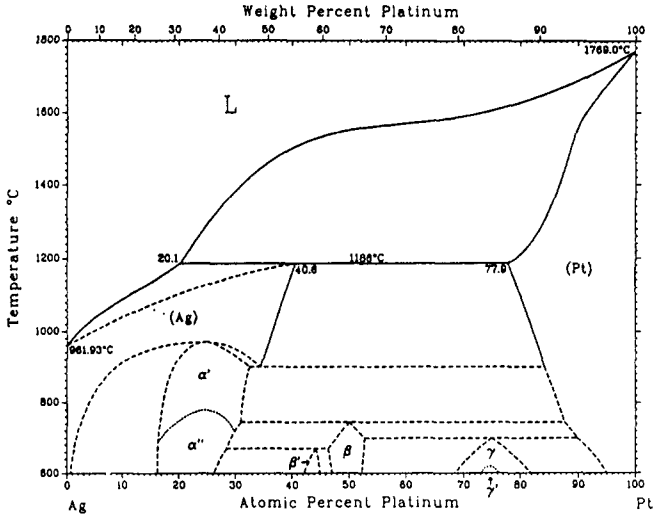

Fig. 1. Ag–Pt binary system according to the compilation of Massalski [1].

2. Experimental

All the alloys (0.3 to 1.0 g) were synthesised by melting pure metals (Ag 99.99% and Pt 99.999%, Metalor, Neuchâtel, Switzerland) in an HF furnace, in sealed silica tubes under an inert atmosphere of pure argon.

The composition of the alloys was controlled by comparison of the weight of pure metal mixtures before and after melting in the induction furnace. The measured tiny loss of metal is attributed to Ag and does not exceed 0.03 at.% Ag in the region richest in silver.

The synthesised alloys are always very malleable and it is impossible to prepare fine powder for XRD measurements, so the determination of spectra are carried out using thin pellets of the alloys, with silicium standard for accurate lattice parameters.

All the other measurements conditions (DTA, XRD and EMPA) on long-time annealed alloys were described in Ref. [3].

3. Results

Fig. 2 includes the thermal arrests on heating by DTA, XRD parameters measurements and microprobe observations as well as the composition of the

* Corresponding author.

PII S0925-8388(96)02257-8

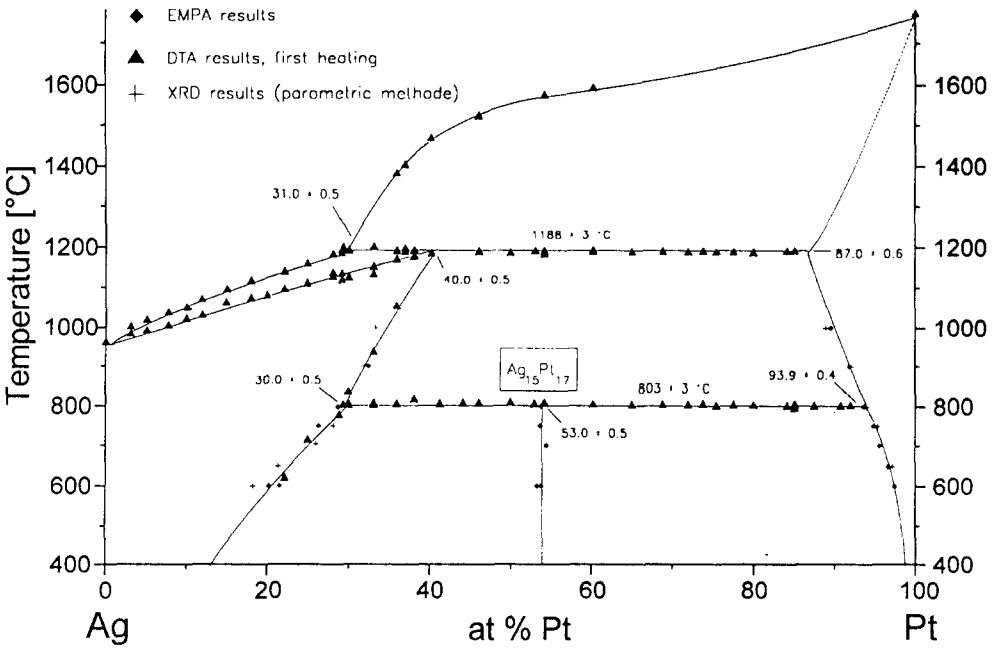

Fig. 2. Ag–Pt phase diagram after our present work, including DTA, XRD and EMPA measurements.

phases. Only one intermediate phase appears at 53 ± 0.5 at.% Pt, stable below 803 ± 3°C. The domain of existence of this phase is very narrow, as confirmed by XRD: two-phase regions at 52 or 54 at.% Pt are detectable with residual diffraction lines, either of α Ag or α Pt random solid solutions (see Figs. 3 and 4). The composition and the narrow region of existence of the $Ag_{15}Pt_{17}$ phase is also confirmed by EMPA measurements and micrography (see Fig. 5).

The determination of the extent of the α-solubility regions in the platinum- and silver-rich range was done using the parametric method:

— Fig. 6 shows the variation of a in the lattice of solid solution, as a function of the composition and the

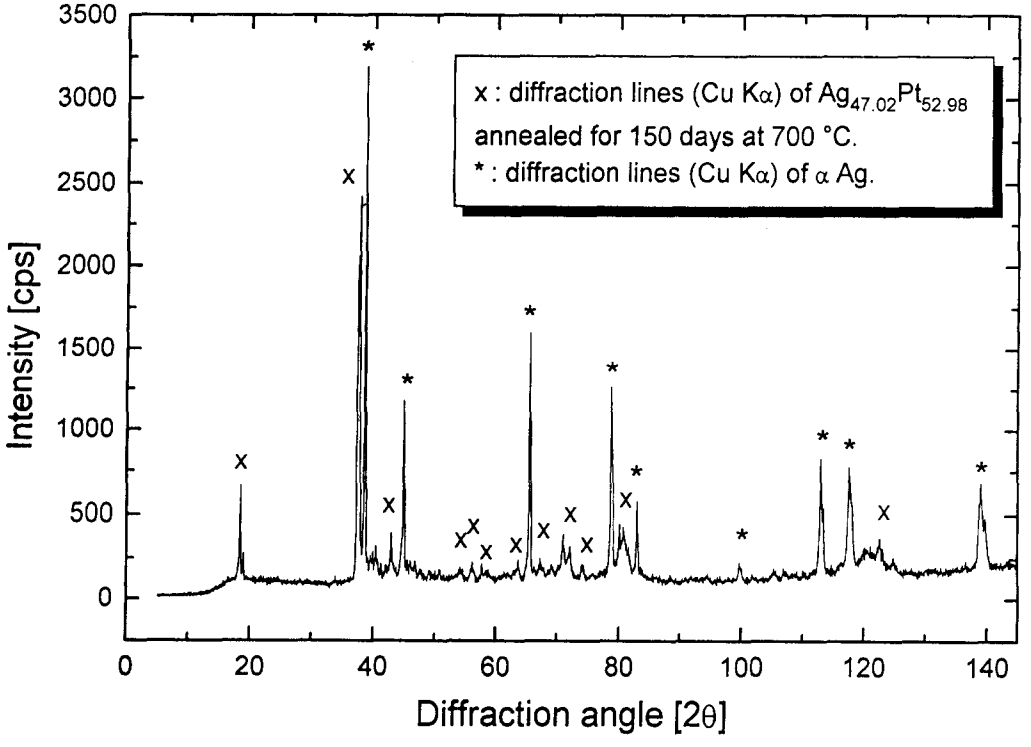

Fig. 3. Measured diffractogram ($\lambda = 1.5405$ Å) of $Ag_{47.02}Pt_{52.98}$ annealed at 700°C for 150 days.

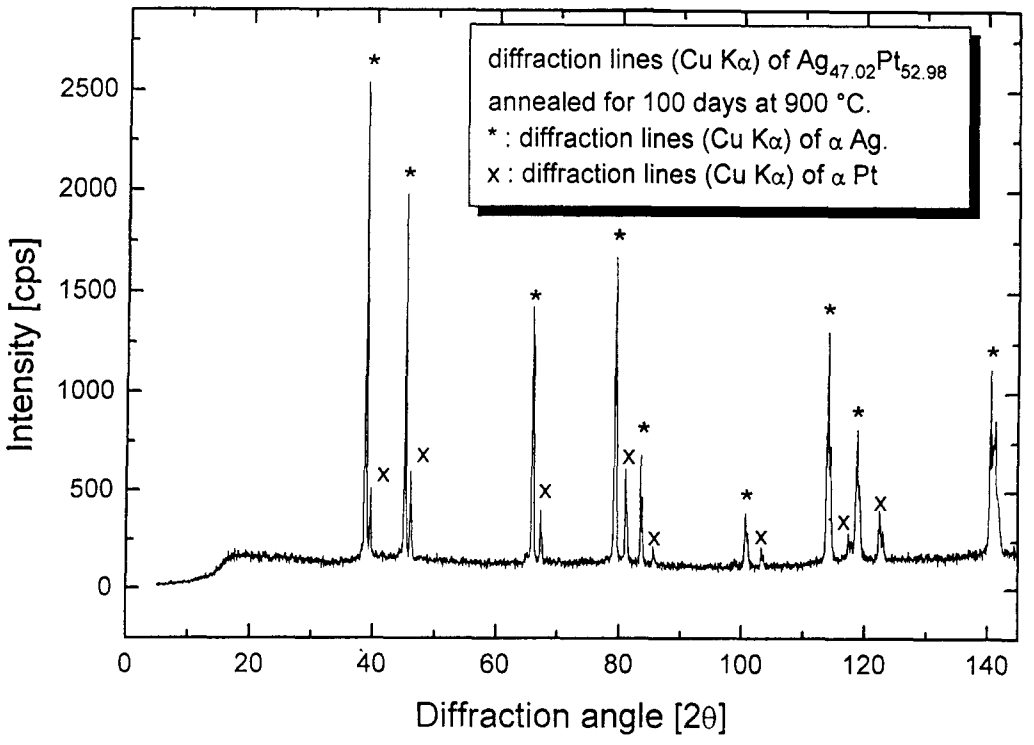

Fig. 4. Pattern of $Ag_{47.02}Pt_{52.98}$ ($\lambda = 1.5405$ Å) annealed at 900°C for 100 days.

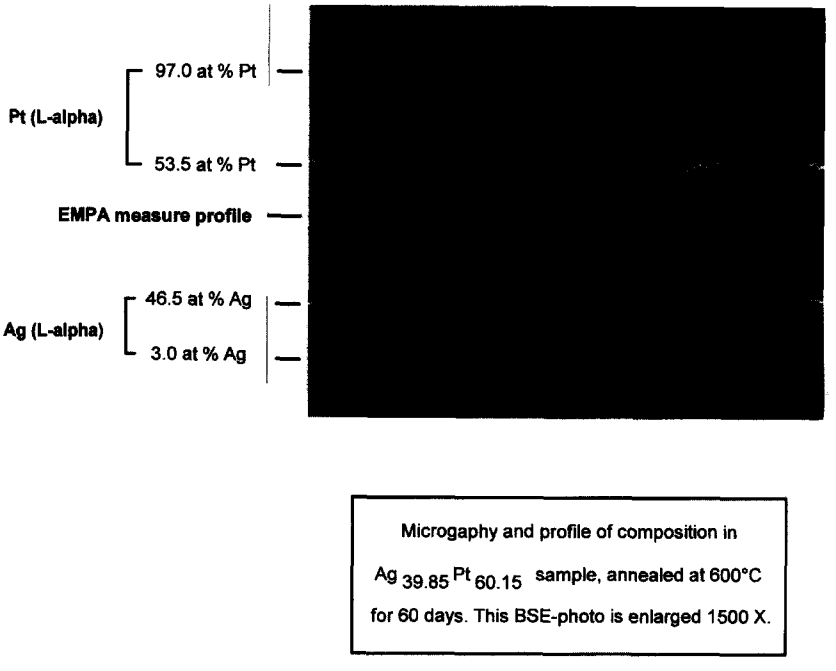

Fig. 5. Micrography and EMPA-profile of composition in $Ag_{39.85}Pt_{60.15}$ sample, annealed at 600°C for 60 days.

annealing temperatures of the alloys, in the silver-rich region. The accuracy of the measurements is of the order of ± 0.001 Å;

— Fig. 7 presents the variation of the lattice parameter *a* as a function of the composition and the annealing temperatures of the alloys, in the platinum-rich region.

Also, the Tamman estimation of the heat absorbed by destruction of $Ag_{15}Pt_{17}$ at 803°C confirms a maxi-

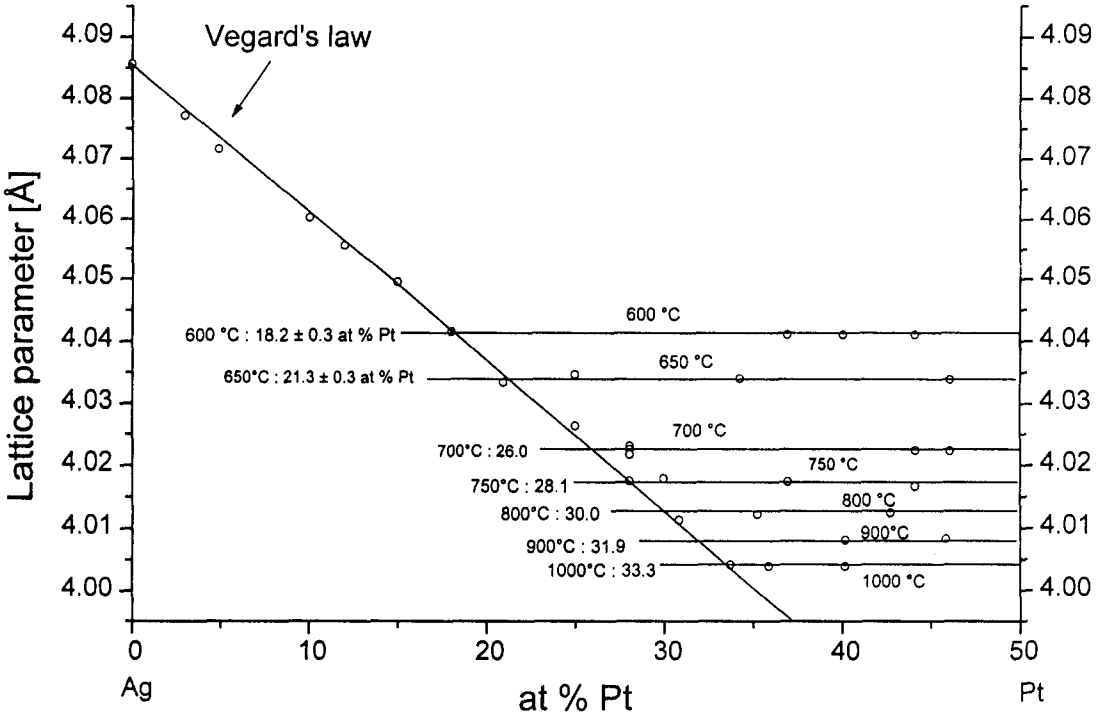

Fig. 6. Variation of the lattice parameter a (f.c.c. structure) in the Ag-rich α-solubility range.

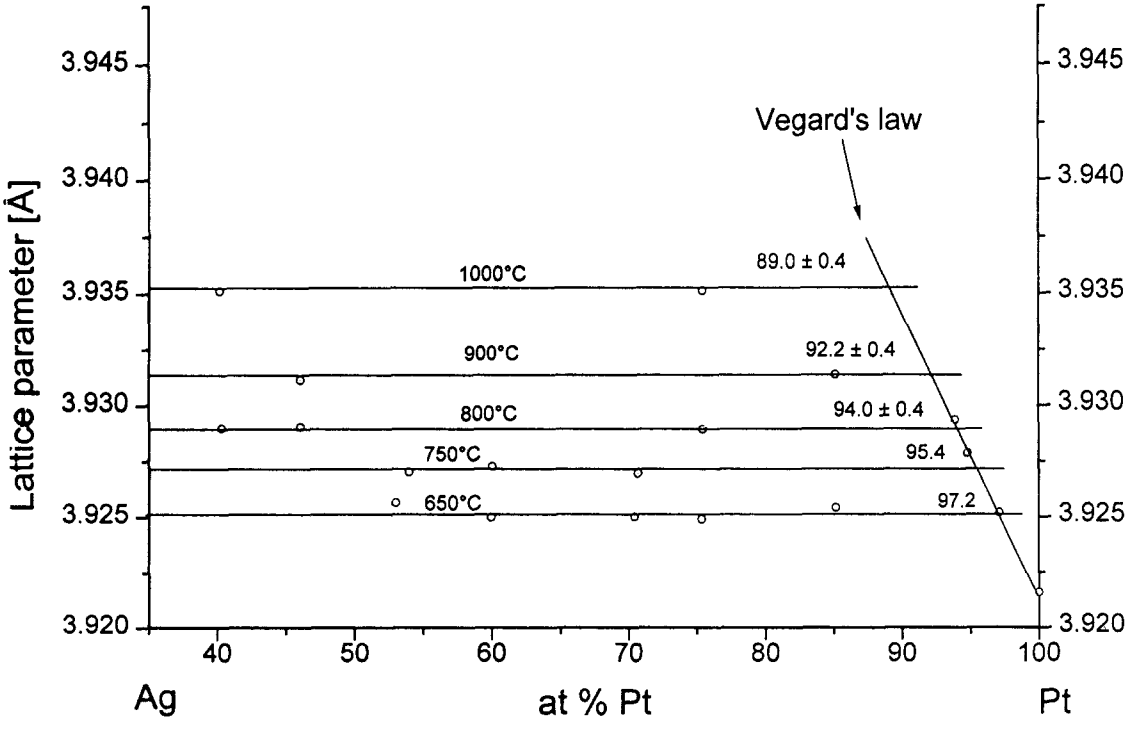

Fig. 7. Variation of the lattice parameter a (f.c.c. structure) in the Pt-rich α-solubility domain.

mum thermal effect (low, about four times less than the peritectic melting of α Ag at 1188 ± 3°C) in the range of 50 to 55 at.% Pt. Fig. 8 indicates the DTA effects at 50.08 at.% Pt for illustration.

We have also detected a slight demixing tendency along the liquidus curve between 1550 and 1650°C.

The XRD and EMPA agree perfectly and underline the presence of a larger solubility of platinum in silver

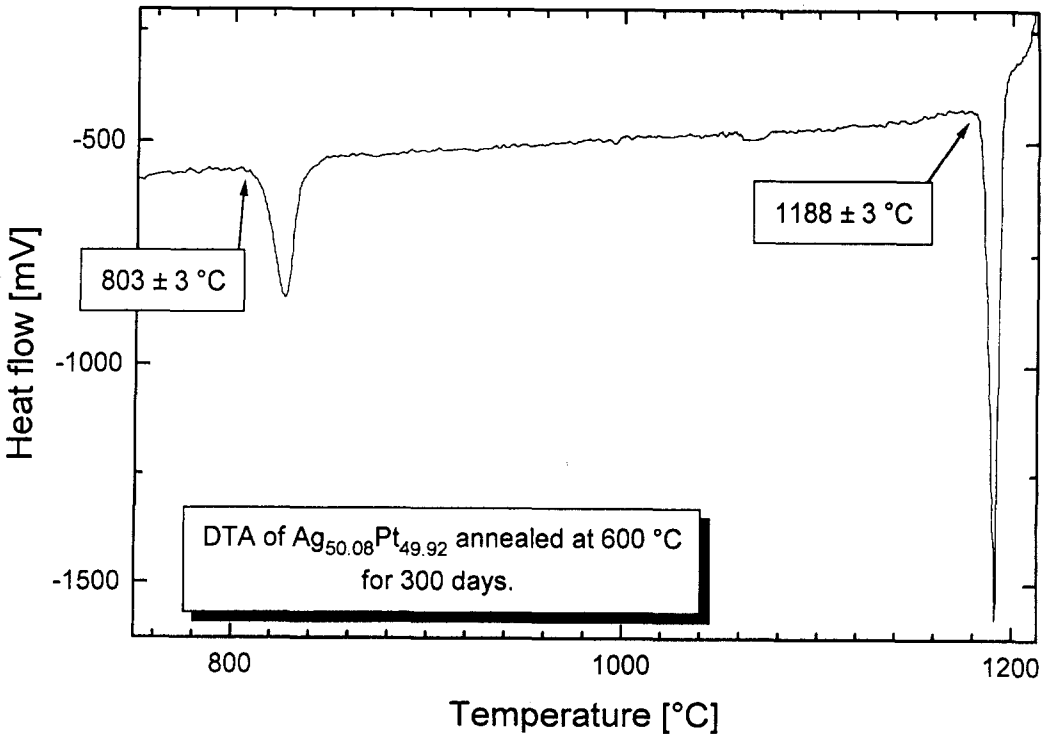

Fig. 8. DTA of $Ag_{50.08}Pt_{49.92}$ annealed at 600°C for 300 days. First heating (5°C min^{-1}) with 110 mg alloy.

(30.0 at.% Pt at 803°C and 40.0 at.% Pt at 1188°C) than that previously proposed in the literature (32.5 at.% Pt at 800°C and 40.6 at.% Pt at 1186°C [1]).

The measured solubility of silver in platinum (α Pt) is also less (93.9 at.% Pt at 803°C and 87.0 at.% Pt at 1188°C instead of 86.0 at.% Pt at 800°C and 77.9 at.% Pt at 1188°C [1]).

4. Discussion

Long annealing times (200 days at 300°C, 150 days at 500°C and 100 days at 800°C) are absolutely necessary in order to obtain reproducible results for the regions containing peritectic transformations as well as for the reproducible detection of the intermediate phase $Ag_{15}Pt_{17}$. The crystal structure of this complicated giant cell could not be determined, lacking the preparation of a monocrystal. Fig. 6 confirms the existence of this new compound, analysed by EMPA. A strong diffraction line at $2\Theta = 16°$ suggests for $Ag_{15}Pt_{17}$ a deformed cubic structure with $a \simeq 8.0$ Å, corresponding to 32 atoms.

The present measurements give an answer to questions raised in Ref. [4]. Our results are in good agreement with the phase diagram calculated by Karataya and Thompson [4] on the Ag-rich side, but at lower temperatures (below 803°C); we have also confirmed the existence of only one intermediate stoichiometric compound formed slowly with both solid solution (31.0 ± 0.5 and 87.0 ± 0.6 at.% Pt). The solid solubility of Ag in Pt is much smaller than previously measured on insufficiently equilibrated alloys.

Acknowledgements

The authors express their gratitude to MM. G. Burri and G. Troillet, of the Institut de Physique expérimentale de l'Université de Lausanne, for the careful EMPA measurements.

References

[1] T.B. Massalski, *Binary Alloys Phase Diagram*, Vol. 3, ASM International, OH, 2nd edn., 1990, p. 2998.
[2] A. Schneider und U. Esch, Das system Silber-platin, *Z. Elektrochem., 49* (2) (1943) 73.
[3] Ph. Durussel and P. Feschotte, The binary system Pb–Pd, *J. Alloys Comp.*, in press.
[4] I. Karataya and W.T. Thompson, The Ag–Pt system (compilated and calculated diagram), *Bull. Alloys Phase Diagr., 8* (4) (1987) 334.