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PHASE RELATIONS IN THE Pt–Ag17.5–Si4.5 TERNARY ALLOY

FAZNA ODVISNOST V TERNARNI ZLITINI Pt–Ag17.5–Si4.5

Grega Klančnik, Primož Mrvar, Jožef Medved

University of Ljubljana, Faculty of Natural Science and Engineering, Department of Materials and Metallurgy, Aškerčeva 12, SI-1000 Ljubljana, Slovenia
grega.klancnik@ntf.uni-lj.si

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An investigation of the Pt–Ag17.5–Si4.5 ternary alloy was carried out. Thermodynamic data on platinum systems are scarce and are mostly based on binary systems. No accurate thermodynamic study of the Pt–Ag–Si ternary system has been published so far. Thermodynamic calculations were used as an indication of the possible phase composition for the investigated platinum-based alloy. The results are based on differential scanning calorimetry (DSC) tests, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM – EDS) and X-ray diffraction measurements (XRD). The analyses revealed the presence of two phases that were found after homogenization at 900 °C: a high-temperature phase, Pt_2Si, and a Ag (Pt) solid solution.

Keywords: Pt–Ag–Si alloys, thermal analysis, thermodynamics

V tem prispevku je opisana raziskava, ki je osredinjena na ternarno zlitino Pt-Ag17.5–Si4.5. Za zlitinske sisteme, ki so osnovani na platini, so termodinamski podatki skopi in temeljijo predvsem na binarnih faznih sistemih. Nobena termodinamska študija še ni bila opravljena na ternarnem sistemu Pt–Ag–Si. Za izbiro ustrezne kemijske sestave smo uporabili termodinamski izračun. Prvi rezultati so bili dobljeni z diferenčno vrstično kalorimetrijo (DSC), rastrskim elektronskim mikroskopom z energijsko disperzivno rentgensko spektroskopijo (SEM – EDS) in rentgensko analizo (XRD). Analize so potrdile obstoj dveh binarnih faz, dobljeni po homogenizaciji na 900 °C. Najdeni fazi sta visokotemperaturna faza Pt_2Si in trdna raztopina na osnovi srebra Ag (Pt).

Ključne besede: Pt-Ag-Si zlitine, termična analiza, termodinamika

1 INTRODUCTION

In this study we have investigated an alloy from the ternary Pt–Ag–Si system with the aim to determine the phase composition of the low-melting platinum-based alloy. Using thermodynamic equilibrium calculations of the phase diagram, an indication of a suitable chemical composition for the alloy can be made. From the analysis of the ternary alloy the investigated new information on the extension of the binary phases into the ternary system was expected. Differential scanning calorimetry, scanning electron microscopy with EDS analyses, and X-ray diffraction measurements were used for the investigation.

2 THEORY

The binary boundary systems of the ternary Pt–Ag–Si system according to the literature are shown in **Figure 1**.[2,3] The Pt–Si binary system is rather complex with several intermetallic phases (Pt_3Si, $Pt_{12}Si_5$, Pt_2Si, Pt_6Si_5 and PtSi). The phases of the binary system Pt–Si are presented in **Table 1**. The Ag–Pt binary system is a

Table 1: The binary phases taken from the Pt–Si system
Tabela 1: Faze v binarnem sistemu Pt–Si

Phase	Space group	Structure type	Lattice parameter /nm			Ref
			a	b	c	
Pt3Si	C12/m1	Pt3Ge	0.7724(2)	0.7767(2)	0.5390(2)	5
HT-Pt3Si	Pnma	Fe3C	0.5579	0.7697	0.5520	6
Pt12Si5	I4/m	Ni12P5	0.9607	0.9607	0.5542	6
HT-Pt12Si5*	P4/nZ	/	0.13404	0.13404	0.5451	7
Pt2Si	I4/mmm	ThH2	0.3933	0.3933	0.5910	8
HT-Pt2Si	P6-2M	Fe2P	0.6440	0.6440	0.3573	8
PtSi	Pbnm	FeB	0.5932(1)	0.5595(1)	0.3603(1)	9
PtSi	Pnma	MnP	0.5595	0.3603	0.5932	9
Pt6Si5*	P121/m1	/	0.15308	0.348	0.6120	10
Pt2Si3	P63/mmc	Sc2O2S	0.3841(1)	0.3841	1.1924(5)	11

* – no data present, HT – high-temperature phase

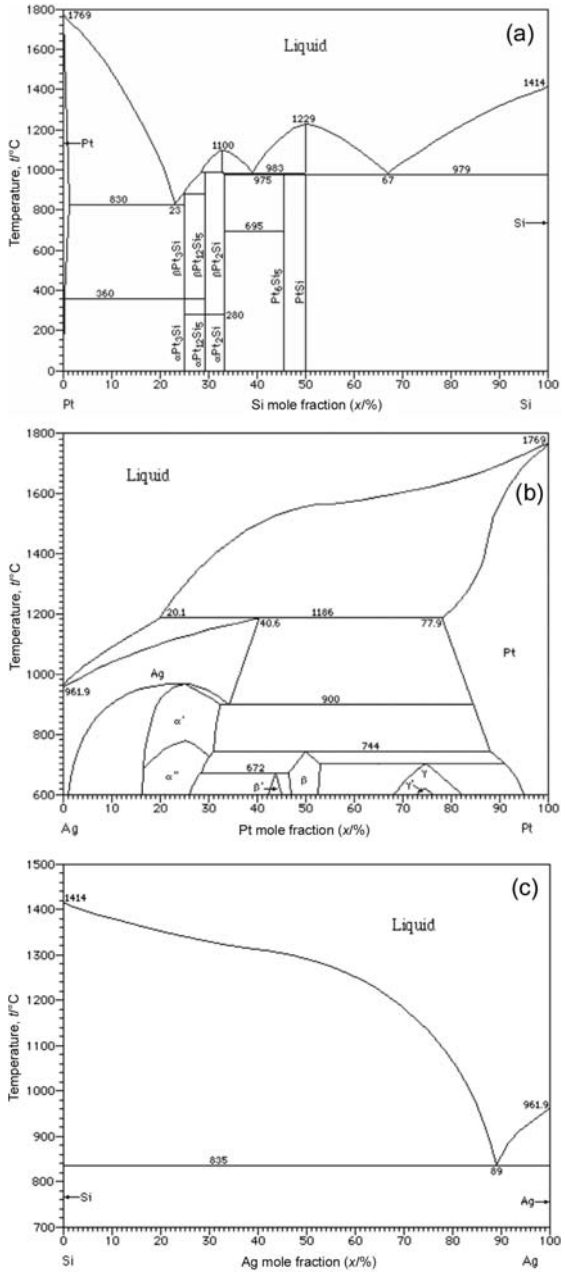

Figure 1: Phase diagrams of the binary systems: Pt–Si[2] **(a)**, Ag–Pt[3] **(b)** and Si–Ag[4] **(c)**

Slika 1: Fazni diagrami binarnih sistemov: Pt–Si[2] **(a)**, Ag–Pt[3] **(b)** and Si–Ag[4] **(c)**

peritectic system with several reactions in the solid state. The Ag–Pt phase diagram assessed by Karakaya and Thompson[3] identified a superstructure at low temperature and a miscibility gap between the silver and the platinum-rich corner.[1] The intermediate phases are known as β (PtAg), γ and γ' (Pt_3Ag). Other phases, such as α', α'' ($PtAg_3$) and β', are also possible. Invariant reactions other than the peritectic are uncertain, because of the lack of conclusive studies. The phase diagram of the Si–Ag binary system is a eutectic type, without intermediate or intermetallic phases.

3 EXPERIMENTAL

The chemical composition of the alloy was selected on the basis of the results of thermodynamic calculations of the liquidus surface for the isothermal section of the ternary system Pt–Ag–Si using Thermo Calc 4 for Windows (TCW 4) with the SSOL4 database.

The composition of the alloy is presented in **Table 2**.

The alloy was melted in a high-purity Al_2O_3 crucible in an argon atmosphere from elements of high-purity grade (99.99). The melting was performed with a high-temperature furnace, where the platinum was heated up to 1800 °C. The temperature control was established with a type-D thermocouple (W- 3 % Re – W- 25 % Re). After adding silver and silicon, the melt was mixed to achieve homogeneity. The alloy was then re-melted and slowly cooled to room temperature. The melting crucible inside the high-temperature furnace is presented in **Figure 2**.

The alloy was investigated with thermal analyses (STA – 449 Jupiter, Netzsch) and X-ray diffraction (XRD) patterns. These X-ray diffraction patterns were recorded at room temperature using Cu Kα1 and Kα2 radiation with a Bruker X8 APEX II CCD diffractometer. The diffraction patterns were compared with those

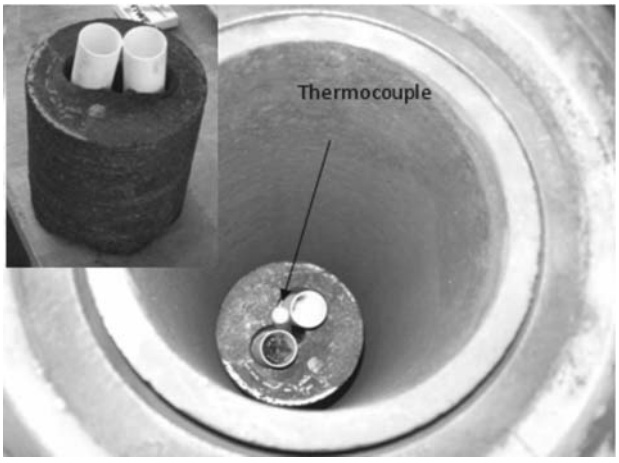

Figure 2: High-temperature furnace and position of the type-D thermocouple

Slika 2: Visokotemperaturna peč in položaj termoelementa tipa D

Table 2: Chemical composition of the investigated alloy

Tabela 2: Kemična sestava preiskovane zlitine

Sample	mass fraction (w/%)			mole fraction (x /%)			mass, m/g		
	Pt	Ag	Si	Pt	Ag	Si	Pt	Ag	Si
1	77.952	17.522	4.526	55.312	22.436	22.277	1.957	0.439	0.113

generated for known compounds and used to calculate the refined unit-cell parameters. The second recording of the X-ray diffraction patterns, using the same radiation, for the aged sample was carried out using PANalytical X-pert PRO MPD for samples with flat surfaces.

The maximum temperature for the STA 449 Jupiter – Netzsch device was 1550 °C for the as-cast sample, with a 20 K/min heating rate up to 1200 °C for the homogenized sample. The measurements were performed in an inert atmosphere of argon, applying the empty crucible as a reference. The heating program for the homogenized sample was as follows: heating at 25 K/min to the homogenization temperature (900 °C), holding for 30 min, and then further heating at 5 K/min up to 1200 °C.

The microstructure was examined on polished specimens using a Jeol 5610 scanning electron microscope (SEM) equipped for energy-dispersive X-ray spectroscopy (EDS). Several EDS point analyses were obtained for each phase.

4 RESULTS

4.1 Thermodynamic calculation

The calculation of the phase diagrams with TCW4 is an important tool for the design of materials and it significantly decreases the amount of experimental work required. The purpose of the thermodynamic calculations was to predict the liquid region inside the ternary Pt–Ag–Si system. The last liquid region served for a determination of the nominal alloy composition with a predominating platinum component (with a minimum content of the mass fraction 50 %). Below a temperature of 1089 °C the thermodynamic calculation predicts the crossing of the liquidus surfaces in the ternary system. **Figure 3** presents the isothermal section of Pt–Ag–Si at 1089 °C, which is the lowest liquidus temperature for an alloy with a content of platinum and the mass fraction of Ag 40 % and 6 % of Si. The composition of the investigated alloy is inside the region of this composition.

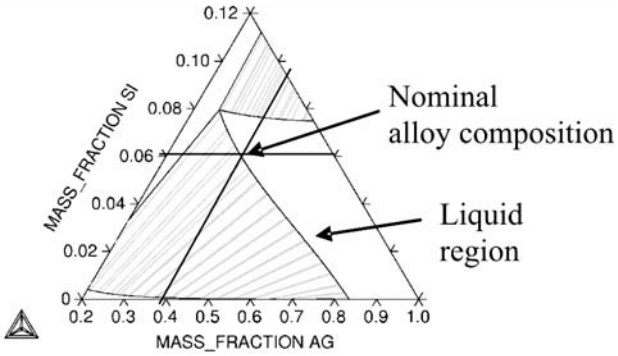

Figure 3: Isothermal section of the Pt–Ag–Si ternary system: liquid region at 1089 °C and crossing of the liquidus surfaces

Slika 3: Izotermni prerez ternarnega sistema Pt–Ag–Si: področje taline pri 1089 °C in prerez liquidusnih ploskev

4.2 Differential scanning calorimetry (DSC)

The aim of the DSC analyses was to determine the characteristic temperatures of possible reactions in the alloy in the temperature interval between 25 °C and 1550 °C. The DSC heating curve is presented in **Figure 4a**.

Two peaks were found on the DSC heating curve in **Figure 4a**, with a total heat of fusion of 89.147 J/g, which is the contribution of two different main reactions. **Figure 4a** represents the melting point at 964 °C with a heat of fusion of 5.887 J/g, with an additional reaction at 969.2 °C. The second main reaction is found at 1044.3 °C, with a heat of fusion of 83.26 J/g. The dislocated first peak away from the second one is assumed to be the result of a minute content of the first melting phase and a distinct temperature difference between the first and second reactions. The presence of a minute content of the first melting phase is also discernable from the values of the enthalpy of fusion (**Figure 4a**). Two peaks were also found on the DSC cooling curve in **Figure 4b**, which are also the contribution of two different main reactions, with a total heat of solidification of 102.726 J/g. The liquidus temperature determined from the cooling curve is at 1019.9 °C, and the solidification occurs with a high undercooling, with a solidification enthalpy of 97.45 J/g for the first reaction. With further cooling to 832 °C an exothermic peak with a small initiation at 853.2 °C and an enthalpy of solidification of 5.276 J/g was found. The high undercooling is discussed in relation to the theoretical liquidus determined from the heating curve. High undercooling usually indicates a lack of nucleation sites inside the melt at the theoretical solidification temperature determined during the heating

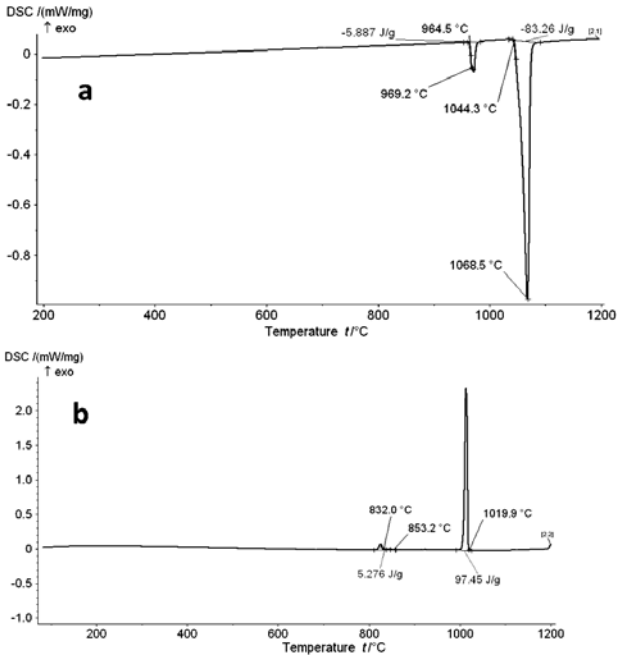

Figure 4: DSC analyses of the alloy: heating **(a)** and cooling curve **(b)**

Slika 4: DSC analiza zlitine: segrevalna **(a)** in ohlajevalna krivulja **(b)**

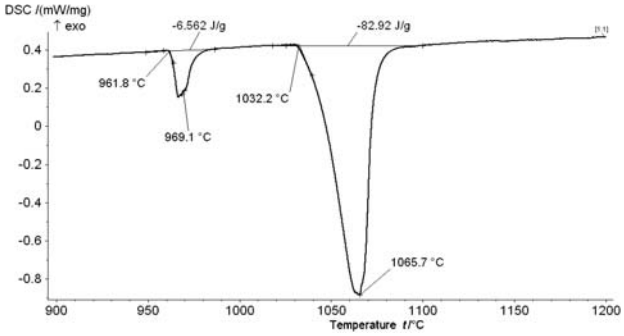

Figure 5: The DSC heating curve of the homogenized sample
Slika 5: DSC-segrevalna krivulja homogeniziranega vzorca

of the same alloy. The nucleation of the liquid during the melting is facilitated by the large number of microstructural defects, such as grain boundaries, especially segregating impurities, and makes the determination of the liquidus more reliable.

The homogenization temperature is selected below the first reaction. For the alloy homogenized at 900 °C, the heating curve between 900 °C and 1200 °C is shown in **Figure 5**. It shows a melting point at 961.8 °C. A reaction was also recorded at 969.1 °C, and the second strong effect was recorded at 1032 °C. The liquidus temperature determined from the DSC heating curve was 1065.7 °C.

4.3 Energy-dispersive X-ray spectroscopy (EDS)

The points of EDS analyses are presented in **Figure 6**. The results for the homogenized sample, gathered in **Table 3**, show a possible intermetal phase matrix based on platinum and silicon, which has been observed already.[2] The mole fraction of platinum in solution in the silver phase is about 2 %. Small deviations in the platinum content inside the silver-based phase are in relation to the reaction at 969.1 °C (spectra 1 and 2 in **Figure 6**). It is confirmed later in this paper that silicon only appears in the Pt–Si system (**Figure 7c**).

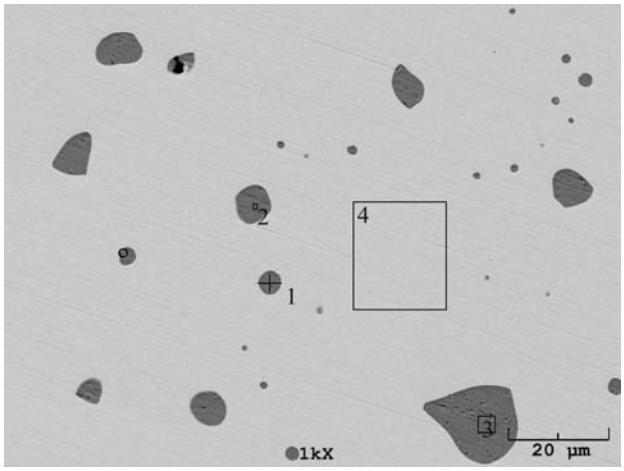

Figure 6: SEM micrograph of the microstructure after homogenization at 900 °C
Slika 6: SEM-mikroskopska slika mikrostrukture po homogenizaciji na 900 °C

Table 3: EDS analyses
Tabela 3: EDS analiza

Specter	Element	mole fraction *x* / %	mass fraction *w* / %
1	Ag	97.51	95.58
	Pt	2.49	4.41
2	Ag	97.55	95.66
	Pt	2.44	4.33
3	Ag	98.43	97.19
	Pt	1.56	2.80
4	Si	26.21	4.93
	Ag	2.57	1.86
	Pt	71.21	93.19

4.4 X-ray diffraction phase analysis (XRD)

The XRD analyses of the homogenized sample confirmed the presence of a small content of a silver-based phase and a larger amount of HT-Pt_2Si (high-temperature) metastable phase (**Figure 7b,c**). The recorded

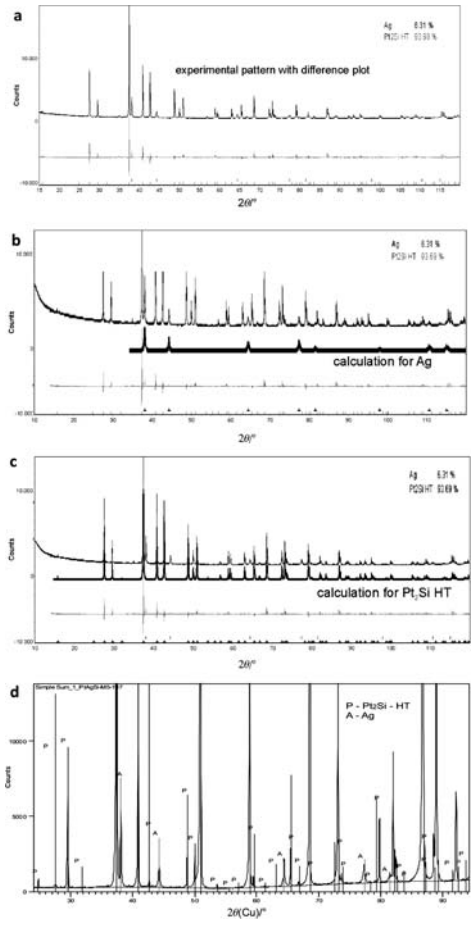

Figure 7: X-ray powder diffraction pattern: experimental pattern (a), silver-based phase (b), HT–Pt_2Si phase (c) and diffraction pattern of the aged sample at room temperature (d)
Slika 7: Posnetki rentgenska praškovne difrakcije: eksperimentalni posnetek (a), srebrova faza (b), faza HT–Pt_2Si (c) in difrakcijski posnetek staranega vzorca na sobni temperaturi (d)

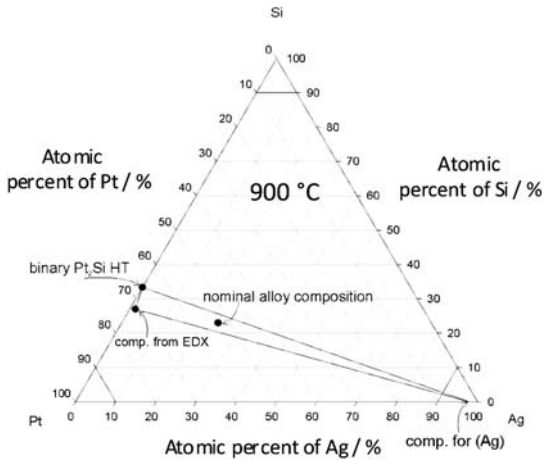

Figure 8: Isothermal section of the Ag–Pt–Si system at 900°C
Slika 8: Izotermni prerez sistema Ag–Pt–Si pri 900 °C

X-ray diffraction pattern of the alloy is shown in **Figure 7a**. The X-ray diffraction pattern recorded again after 2 months of aging at room temperature for possible changes in the HT Pt_2Si phase revealed the presence of a high-temperature phase HT-Pt_2Si and a silver-based phase (**Figure 7d**).

5 DISSCUSSION

After homogenization at 900 °C the melting point was at 961.8 °C, and near to the melting point of silver. The EDS analyses confirmed the presence of the silver phase with a small content of platinum. The EDS analyses also revealed a phase with a high content of platinum. The X-ray diffraction patterns after homogenization at 900°C revealed the existence of two phases: a silver-based phase and a HT-Pt_2Si phase. The determined lattice constant for the silver-based phase is 0.408364(18) nm. The lattice parameter for silver is at 0.40857 nm, with an Fm-3m space group. The determined HT–Pt_2Si phase has a lattice parameter a = 0.6460310(45) nm and b = 0.3577385(45) nm with a P6-2m space group. The literature, shows that the HT–Pt_2Si or the β–Pt_2Si is a congruent phase with the following lattice parameters: a = 0.6436 nm and c = 0.3569 nm or a = 0.6440 nm and c = 0.3573 nm. Thus, similar values to those in our investigation. From **Figure 8** it can be concluded that the nominal alloy composition in mole fractions (55.36 % Pt, 22.43 % Ag, 22.27 % Si) is really a two-phase region of the silver-based phase and the HT-Pt_2Si phase inside the Gibbs concentration triangle between the silver-rich corner and the binary Pt_2Si phase.

6 CONCLUSIONS

After homogenization at 900 °C the Pt–Ag17.5–Si4.5 ternary alloy was characterized by the presence of two compounds: the HT–Pt_2Si phase and a silver-based phase. It can be concluded from the X-ray diffraction patterns, the EDS and the DSC that the alloy with mass fractions 17.5 % of silver and 4.5 % of silicon has a melting point at 961.8 °C as a result of the melting of the silver-based phase. The effect at 1032 °C, determined from the DSC heating curve, is related to the melting of the HT-Pt_2Si phase and the liquidus temperature of the alloy is at 1065.5 °C.

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