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THERMODYNAMIC PROPERTIES OF Ag-Pt ALLOY MEASURED USING A SOLID ELECTROCHEMICAL METHOD

Although Ag-Pt system is crucial for several technological applications, investigations of the thermodynamic properties of this system are limited. In the present study, activity of silver at various temperatures in the platinum rich solid solution was measured by a solid electrochemical method and employing AgI as the solid electrolyte. The EMF was determined using a galvanic cell $(-)|Ag|AgI|Ag-Pt\ alloy|C|Pt(+)$, which provided novel experimental data on thermodynamic properties of a Ag-Pt alloy. Activity, partial molar of Gibbs energy, enthalpy and entropy of silver in a solid solution containing 1 at % Ag between 573 and 673 K have been calculated. The results indicated that the activity of silver obtained in the present study shows a large positive deviation from the ideal Raoultian behavior. Microstructures of alloys with different compositions were also compared.

Keywords: silver conducting electrolyte, EMF method, Silver, Platinum, Thermodynamics

1. Introduction

Platinum, grayish white metal, is used for a wide range of applications in the human life. Because of its capability to absorb gas, Ag-Pt system plays an important role mainly as a catalyst. In automotive it is used as CO_2 emission control. In chemical and petroleum industries it is employed as a booster of refining and reforming processes [1]. The ability to understand the behavior of the Ag-Pt system is the key of the success for process optimization during the production and recovering of the metal through metallurgical routes. Although the Ag-Pt system is essential for a wide range of industrial applications, the knowledge of its thermodynamic properties describing the behavior of the metal alloy is very limited.

Doerinckel [2] determined the liquidus, solidus lines and peritectic temperature of the Ag-Pt system. The transformation of liquid and platinum rich phases (δ) to silver-rich terminal phase (α) at peritectic temperature was reported at 1457 K. Based on the phase diagram he reported, the maximum solubility of platinum in the silver rich phase is around 35.7 at % at 1457 K. The investigation by Johansson and Linde [3] indicated new intermetallic phases (β, γ', γ) are formed below 1023 K through a peritectoid reaction. This finding of stable intermetallic phases at low temperatures was also supported by Schneider and Esch [4] who suggested the formation of a new intermetallic compound (Ag_3Pt), and an intermetallic phase (δ') in the platinum-rich side (δ).

However, investigation by Novikova and Rudnitskii [5] indicated that there was no intermetallic phases, except the silver-rich (α) and platinum-rich (δ) terminal phases in the Ag-Pt system. They also investigated the microstructure of tempered alloys in the Ag-Pt system over a wide range of compositions, between 5 and 97.6 at % Ag. The samples were tempered at selected temperatures and cooled at a rate of 100 K per day. It showed that in the microstructure of alloy containing 5 at % Ag after being tempered at 1173 K for 100 hours, the platinum-rich phase (δ) existed with second phase, i.e. a silver-rich phase (α) which was formed inside and on grain boundaries of the platinum-rich phase (δ). Also, platinum-rich phase (δ) was formed in the silver-rich phase (α) of the tempered alloy containing 97.6 at % Ag. This study suggested that at room temperature, the solubility of silver in the platinum-rich alloys and the solubility of platinum in the silver-rich phase are less than 5 and 2.4 at %, respectively.

Karakaya and Thompson [6] assessed the phase diagram which showed a good agreement with previous reported experimental data [2-4]. However, the presence of intermetallic phases ($\beta, \gamma', \gamma, \delta'$) was disregarded since there were still disagreements among the authors [2-5] about the stability of these intermetallic compounds. They also modelled the thermodynamic properties of the liquid and solid solutions in the system. Mixing enthalpy of the liquid phase was reported to be positive in the whole range of composition. Whereas, in the solid solution, negative mixing enthalpy only existed in the silver-rich terminal phase. The activity of silver at 1173 K was predicted to behave nonideally and to have a positive deviation from Raoult's Law.

Moreover, a new intermetallic, $Ag_{15}Pt_{17}$, was reported by Durussel and Feschotte [7] who investigated the system by using equilibration, DTA, X-ray diffraction and EPMA (electron

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probe micro analyzer) methods. The samples were equilibrated in silica ampoules sealed under argon atmosphere. Silver-rich (α) and platinum-rich (δ) terminal phases were reported to coexist between 1076.3 and 1461.3 K. $Ag_{15}Pt_{17}$ was seen to decompose to platinum and silver rich phases upon heating at peritectoid temperature which was found to be 1076.3 K. Equilibration time was reported to be 200 days at 573 K in order to obtain reproducible data for the peritectic reaction and detection of $Ag_{15}Pt_{17}$ intermetallic compound. The examination of samples indicated that at the peritectic temperature, which is 1461.3 K, silver dissolves up to 13 at % in the platinum-rich solid solution. Whereas, in the silver-rich phase, silver can dissolve platinum up to 40 at %. The liquidus data determined by DTA was only measured for silver concentrations in the mixture below 62 at %. The reported phase diagram indicated that the solubility of silver in the platinum-rich alloy was about 5 at % at 873 K. At 673 K, and the solvus point was predicted to dissolve 2.5 at % Ag. Thus, below 673 K, the solubility t of Ag in solid Pt was expected to be less than 2.5 at % as indicated by the diagram drawn by Okamoto [8].

An investigation of the Ag rich solid solution by Erni et al. [9] concluded that the Ag_3Pt compound, suggested by Schneider and Esch [4], did not exist in the Ag-Pt system. This was also supported by Sluiter et al. [10] who used an Ab Initio calculation method to examine the Ag-Pt system. They suggested that Ag_3Pt and $AgPt_3$ phases with ordered structures did not exist. The Ag-Pt system was predicted to form a miscibility gap at high temperatures between silver and platinum rich liquids. Mixing enthalpy of Ag-Pt mixture was calculated to be positive in the whole range of compositions. Ab initio calculations were also used by Hart et al. [11] who suggested two new intermetallic compounds, Ag_7Pt and Ag_3Pt_2, to be stable in the Ag-Pt system. They did not, however, measure the saturated phase compositions in the terminal solutions.

Fig. 1 shows a calculated phase diagram of the Ag-Pt system by MTDATA (a thermodynamics and phase equilibrium software from NPL, UK) and SGTE solution database (5.2, November 2015) [12], which suggests that only solid phases of silver and platinum rich alloys with same FCC structure exist, without any intermetallic compounds. This is, however, contrary to the recent careful analysis by Hart et al. [13] about the stabilities of intermetallics in the system at low temperatures.

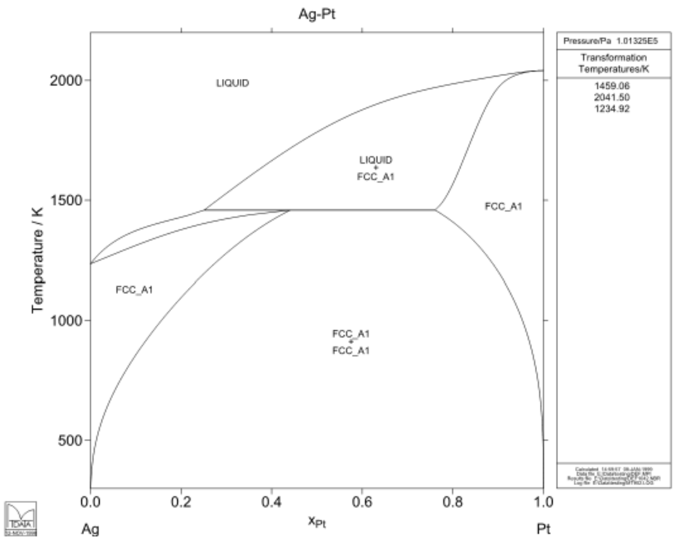

Fig. 1. Phase diagram in the Ag-Pt system [12]

It is evident that although many experimental data on phase boundaries in the Ag-Pt system are available, there is a significant lack of experimental data on the thermodynamic properties such as activity, Gibbs energy, entropy and enthalpy of mixing. Therefore, the thermodynamic property data obtained from the modelling cannot be compared with the experimental observations for validation. In the present study, microstructures of annealed Ag-Pt alloys at different compositions were examined. Activities of silver in a platinum rich alloy were measured by using an improved solid state EMF method. Thermodynamic properties of silver in the solid terminal solution of platinum were then calculated.

2. Experimental technique

The activities of silver in the solid Ag-Pt alloy were measured by using EMF method with solid AgI as the electrolyte. Since AgI melts at 831 K and becomes soft at above 746 K, the experiments were conducted between 573 and 673 K. It was reported that the conductivity of AgI increases significantly within this temperature range [14-16].

2.1. Materials

High purity chemicals were used to synthesis the alloys at different compositions, i.e. 1, 9, 65, and 94 at % of silver. Silver powder (99.96% purity, Alfa Aesar) and platinum powder (99.99% purity, Alfa Aesar) were weighted and mixed carefully in an agate mortar to make 0.25 g mixtures. The mixtures were then pressed using a 0.5 GPa pressing tool to form a pellet of 4 mm diameter and 1.5 mm thickness. The samples were annealed under argon atmosphere in alumina crucibles at 1573 K for 1 day in a horizontal Lenton tube furnace, then cooled to 1173 K and annealed for second time at 1173 K for 2 days. The furnace was initially flushed with Ar gas containing 5% H_2 to remove the traces of oxygen. When the annealing was completed, the samples were cooled in argon stream at a rate of 4 K per minute. AgI powder (99.999%, Alfa Aesar) used in EMF measurement as electrolyte was also pressed to form of a pellet with a same size as the alloy electrode.

2.2. Phase characterization

The synthesized samples were then examined carefully for the homogeneity and chemical composition by using scanning electron microscope (SEM, A LEO 1450, Carl Zeiss Microscopy GmbH, Germany) and Electron Probe Micro-Analyzer

(EPMA, CAMECA SX100, France) with wavelength dispersive spectrometers (WDS), housed at Geological Survey of Finland (GTK). The atomic number, absorption and fluorescence corrections (ZAF correction provided by Cameca) were used. Ag Lα (pure Ag metal) and Pt Lα (pure Pt metal) were employed as silver and platinum standards, respectively. The selected accelerating voltage was 20 kV for the microanalyser operation.

2.3. Apparatus

The cell arrangement adopted in the present study was the same as in the previous studies that successfully investigated other intermetallic systems [17-19]. The schematic illustration of the cell arrangement inside the horizontal tube furnace is presented in Fig. 2. Pure silver reference (99.96% purity, Alfa Aesar), solid electrolyte and test electrode were placed in contact and covered by a carbon disk in the both ends. The cell was inserted in an alumina crucible and placed into a fused quartz working tube of the horizontal furnace (Lenton type LTF 12/50/610). The carbon disks were included to avoid possible reactions between the platinum-rich alloy sample and the platinum lead wire. Two alumina sheaths, with a hole for a platinum resistance thermometer insertion, were placed in the center of the bottom of the alumina crucible and in the other end, and then pressed by strings to ensure that all parts of the cell were in good electrical contact. Both of the furnace ends were sealed by quartz heads with a silicon grease and were having small holes for inlet and outlet of high purity (99.9998%, AGA, Finland) argon gas flow. To achieve nearly static condition, 8 mL per minute of Ar flow (STP) was set.

2.4. Temperatures and EMF Measurement

Temperatures of both ends of the EMF cell were measured by PT100 sensors (platinum resistance thermometers, PRT). The melting point of ice was adopted to periodically calibrate the thermometers. To avoid thermal voltages, the minimum absolute temperature difference less than 1 K between two ends of the cell must be obtained. It was achieved by adjusting the location of the cell in the optimum position in the hot zone of the EMF furnace. The EMF of the cell was measured by using identical platinum wires connected to an electrometer ($2\cdot10^{14}\ \Omega$ input impedance) that allowed to measure the voltage in a reversible way. The lead wires for temperature and EMF measurements were connected to a KEITHLEY-2000 multimeter and KEITHLEY-6517B electrometer (high resistance voltmeter) data logging programs, respectively, to continuously record the signals every 5 seconds.

A cell with pure silver both as reference and test electrode was built to check the reliability of the cell. When silver was used as cathode and anode, zero EMF value is expected. After zero value was obtained, with identical arrangement, the platinum rich alloy (1 at % Ag) was used as the test electrode. The system was considered to reach equilibrium when the EMF remained constant (a scatter of less than 0.1 mV) for more than one day (24 h). To examine that the data obtained from the present study was reproducible and to evaluate possible systematic errors from the measurement, another independent and identical cell with same sample and design but in a different furnace, and different instrument (type and series of the instrument remained the same) was constructed. The results indicated a good agreement.

3. Electrochemical Cell

The electrochemical cell assembled with pure silver as a reference electrode, platinum rich alloy containing 1 at % Ag as a test electrode, AgI as the solid electrolyte, carbon as separator between each electrode and the external circuit, i.e. the platinum wire, can be written in a form of cell notation as

$$(-)Pt|C|Ag|AgI|Ag-Pt\ alloy|C|Pt(+) \tag{1}$$

The vertical bar (I) indicates the presence of an interface between two different solid phases that are in physical contact. The half reactions in the anode and cathode can be expressed by equations (2) and (3), respectively.

$$Ag(fcc) = Ag^{+} + e^{-} \tag{2}$$

$$Ag^{+} + e^{-} = Ag[Pt] \tag{3}$$

The total virtual cell reaction for transferring of silver ions from anode (pure silver) to cathode (a platinum alloy) is therefore:

$$Ag = Ag[Pt] \tag{4}$$

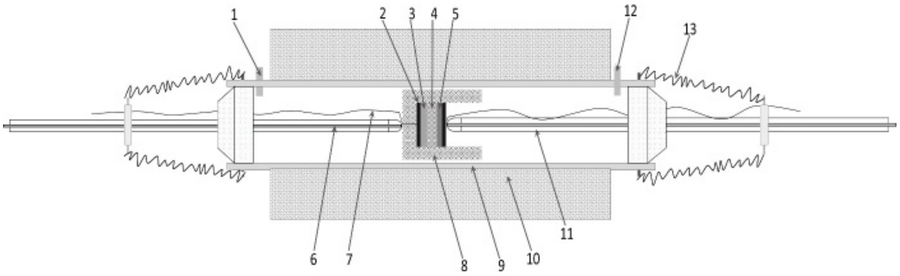

Fig. 2. Schematic arrangement of the cell (not to scale), (1) gas inlet channel, (2) carbon disk, (3) test electrode, (4) electrolyte, (5) reference electrode, (6) resistance thermometer, (7) Pt wire, (8) alumina crucible, (9) quartz tube, (10) tube furnace, (11) alumina sheath, (12) gas outlet channel, (13) loaded spring

Thus, the partial molar Gibbs energy of mixing which is the difference between the chemical potentials of silver in the alloy ($\mu_{Ag[Pt]}$) and pure solid silver (μ^o_{Ag}) is:

$$\Delta_r \bar{G}_{Ag} = \mu_{Ag[Pt]} - \mu^o_{Ag} = RT \ln a_{Ag[Pt]} \tag{5}$$

where $a_{Ag[Pt]}$ is the activity of silver in the platinum-rich alloy, T is temperature (in K) and R is the gas constant ($R = 8.314$ JK^{-1} mol^{-1}). Since the Gibbs energy of reaction is equal to the amount of work other than volume work and only electrical work of one mole ion transfer of silver to the alloy occurs in the system, the Gibbs energy of reaction is also equal to

$$\Delta_r \bar{G}_{Ag} = RT \ln a_{Ag[Pt]} = -nFE \tag{6}$$

where, F is the Faraday constant ($F = 96485.34$ C mol^{-1}) and n is the number of electrons exchanged in the virtual cell reaction (n = 1). Activity of silver in the alloy with solid pure silver as standard state, is then derived from equation (7).

$$a_{Ag} = e^{\frac{-FE}{RT}} \tag{7}$$

From basic thermodynamics, at constant pressure it is known that

$$\Delta_r \bar{G}_{Ag} = -nFE = \Delta_r \bar{H}_{Ag} - T\Delta_r \bar{S}_{Ag} \tag{8}$$

Thus, the partial thermodynamic properties of silver in the measurements can be presented as

$$\Delta_r \bar{H}_{Ag} = nF\left(\frac{dE}{dT}T - E\right) \tag{9}$$

and:

$$\Delta_r \bar{S}_{Ag} = nF\frac{dE}{dT} \tag{10}$$

where $\Delta_r \bar{H}_{Ag}$ and $\Delta_r \bar{S}_{Ag}$ are the partial molar enthalpy and entropy change of reaction (4), respectively. It can be seen that $\Delta_r \bar{H}_{Ag}$ and $\Delta_r \bar{S}_{Ag}$ are proportional to the intercept and the slope of of the E versus temperature plot.

4. Result and discussion

Different backscattered SEM images of the microstructures of annealed samples from various silver concentrations in the initial bulk composition are presented in Figs. 3-6. The chemical analysis obtained by EPMA is presented in Table 1. Microstructural analysis is needed to check the homogeneity of the samples. One phase only present in the alloy is required in order to measure the properties of silver in platinum solid solutions using solid EMF method. If the sample contains, for example, platinum-rich alloy and another phase, as reported by previous study [7], time taken to reach equilibrium between these two phases can be as long as 100 days.

TABLE 1

Chemical compositions of the mixtures and alloy measured by EPMA

Alloy Sample	Initial Composition (At %)		Phase composition after annealing and cooling (at %)				Remark
			Pt Rich Alloy		Ag Rich Alloy		
	Ag	Pt	Ag	Pt	Ag	Pt	
1	94	6	46.02	53.98	94.48	5.52	Not Homogeneous
2	65	35	11.73	88.27	66.7	33.3	Not Homogeneous
3	9	91	11.68	88.32	56.99	43.3	Not Homogeneous
4	1	99	0.97	99.03	Not observed		Homogeneous

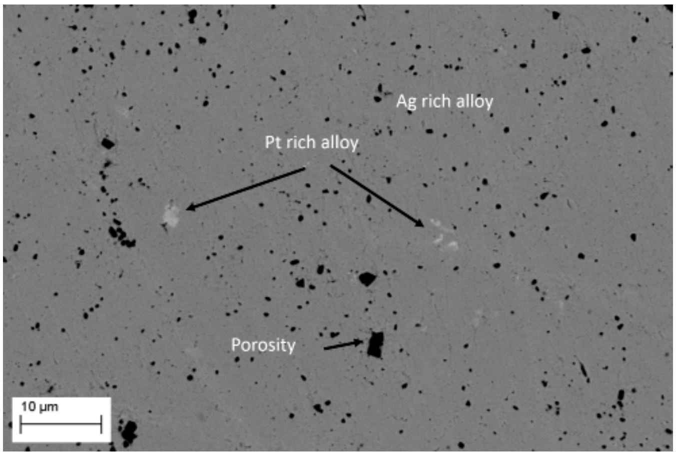

Fig. 3. Microstructure of an annealed alloy made of 94 at % Ag in the initial bulk composition

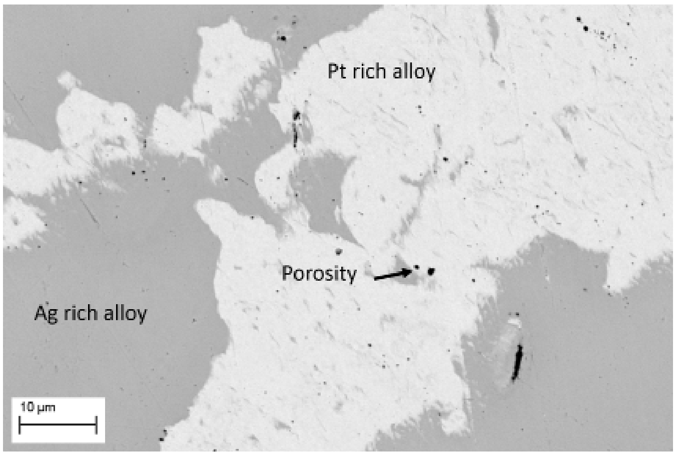

Fig. 4. Microstructure of an annealed alloy made of 65 at % Ag in the initial bulk composition

The microstructures of Ag-Pt alloys were obtained by cooling the sample at a slow rate by which the formation of different phases at low temperatures (i.e below 1173 K) were intended. Fig. 3 shows the microstructure obtained from a cooled sample with 94 at % Ag in platinum. It showed that the silver-rich phase dominates the matrix. The Pt concentration in the silver-rich phase is 5.5 at% which is close to Pt concentration in the initial mixture. However there is still micro crystal of a platinum-rich phase in the annealed sample. When the silver concentration in

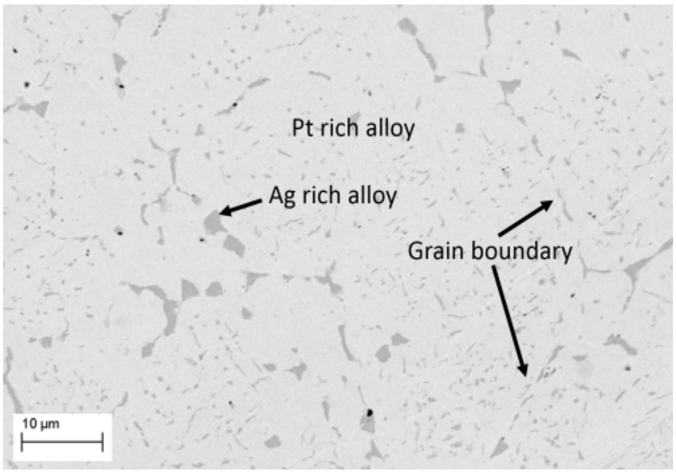

Fig. 5. Microstructure of an annealed alloy made of 9 at % Ag in the initial bulk composition

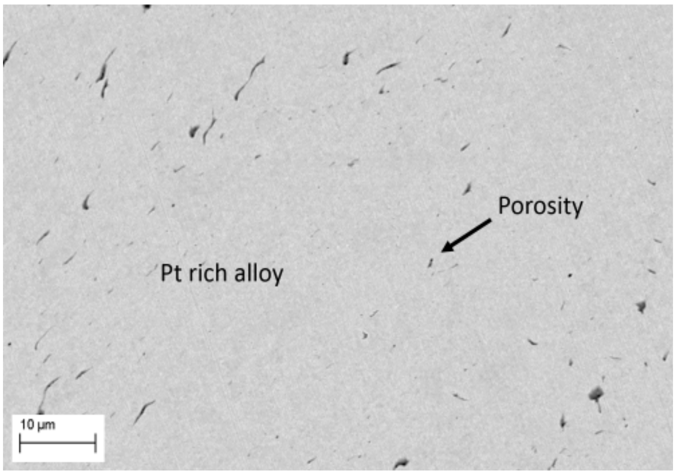

Fig. 6. Microstructure of an annealed alloy made of 1 at % Ag in the initial bulk composition

the initial bulk mixture was reduced to 65 at %, the immiscibility between these two phases is very obvious, as indicated in Fig. 4. Based on the phase diagrams reported by Durussel and Feschotte [7] and Hart et al. [13], during melting a liquid and platinum-rich alloy will form at 1573 K. The Pt concentrations in liquid and platinum-rich alloys are around 33 at% and 92 at%, respectively. When the sample is cooled and equilibrated at 1173 K, silver and platinum-rich alloys will form. The concentration of Pt in the silver-rich and platinum-rich alloys are still 33 at% and 92 at%, respectively. Platinum concentration in the silver-rich and in platinum-rich alloys obtained in the present study are 33.3 at% and 88.27 at%, respectively. Fig. 5 shows a microstructure of the alloy made by mixing 9 at % Ag in platinum. It can be seen that the silver-rich phase still exists. The crystals are formed in the matrix and along the grain boundaries of the platinum-rich alloy. This result agrees with that reported by Novikova and Rudnitskii [5]. However, when Ag in the initial mixture is only 1 at %, the phase is found to be homogeneous. The microstructure is presented in Fig. 6. Therefore, only the alloy with 1 at % Ag was employed for the EMF study between 573 and 673 K, for measuring directly the activity of silver in the platinum-rich alloy.

The obtained EMF values during the experiment at different temperatures are presented graphically in Fig. 7. It shows that the first equilibrium point at 624 K was reached after 350 hours equilibration. Once the first equilibrium was attained, temperature was then changed. Heating and cooling series were adopted to check if the experimental cell is reversible. It can be seen that the next equilibrium was reached in a shorter time than the first one, even though the equilibration temperature was lower.

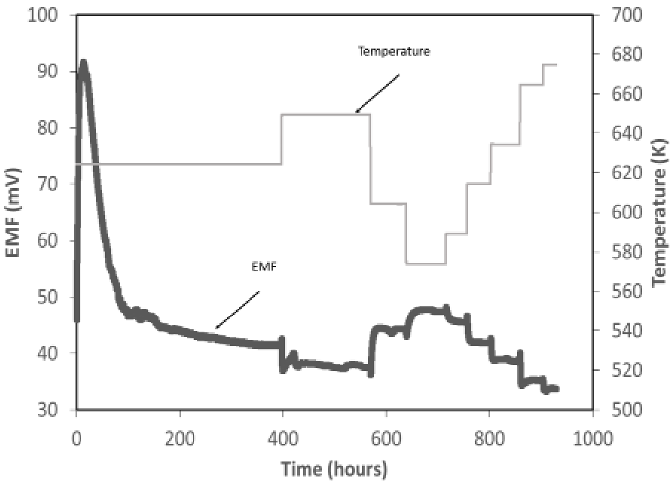

Fig. 7. EMF (mV) of the cell over equilibration time (hour) at different temperatures (K) of the single composition alloy made from 1 at % Ag in the initial bulk composition

Since the EMF values of the alloy containing 1 at % Ag remained constant for more than 24 hours at different temperatures, it means that the cell can reach equilibrium. It includes the equilibration of the alloy at 573.90 K. It means that at 573.90 K, in the Ag-Pt phase diagram the terminal Ag concentration in the platinum-rich alloy is 1 at % or higher.

The measured electromotive forces of the cell at different equilibration temperatures are presented in Table 2 and Fig. 8,

TABLE 2

EMF of the cell at different temperatures from cell 1 and 2, for an alloy containing 1 at % Ag and 99 at% Pt

Temperature, (K)	**Emf, (mV)**	**Cell**
573.90 ± 0.002	47.60 ± 0.003	1
588.90 ± 0.007	45.58 ± 0.011	1
604.08 ± 0.003	44.21 ± 0.005	1
614.16 ± 0.006	41.95 ± 0.003	1
624.25 ± 0.009	41.40 ± 0.06	1
634.28 ± 0.005	38.89 ± 0.006	1
649.36 ± 0.011	37.82 ± 0.015	1
664.48 ± 0.009	35.18 ± 0.05	1
674.50 ± 0.005	33.70 ± 0.004	1
583.40 ± 0.005	45.63 ± 0.006	2

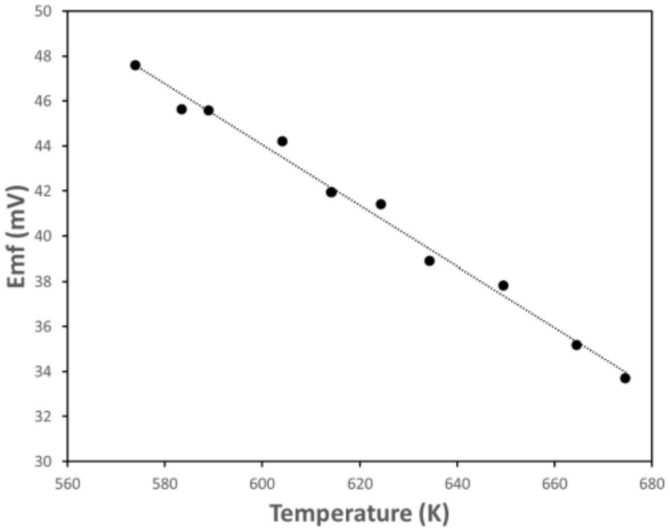

Fig. 8. The EMF of the cell (mV) as a function of temperature (K)

including the uncertainties of each measurement, reported as standard deviations of the EMF readings. The temperature dependence of the cell EMF obeys analytical equation (11) which shows the slope, intercept and the square of correlation coefficient (R^2), i.e. determination coefficient of the straight line, as;

$$\begin{aligned}\text{Emf (mV)} &= (125.26 \pm 2.9615) + \\ &- (0.1353 \pm 0.0048)\,T;\ \ R^2 = 0.9902 \qquad (11)\end{aligned}$$

By using (Eq. 11), the partial molar quantities of silver in solid platinum at different temperatures was calculated and presented in Table 3.

TABLE 3

Thermodynamic properties of a Ag-Pt alloy
(1 at % Ag)

Temperature (K)	Partial Gibbs Energy of Mixing ($\Delta\bar{G}_{rAg}$), (J mol^{-1})	a_{Ag}
573	–4605	0.38
583	–4475	0.40
593	–4344	0.41
603	–4213	0.43
613	–4083	0.45
623	–3952	0.47
633	–3822	0.48
643	–3691	0.50
653	–3561	0.52
663	–3430	0.54
673	–3300	0.55

The activity data in Table 3 shows that activity coefficient of silver at low concentrations (1 at %) in solid platinum is far above the unity. It also indicates that the activity of silver in the alloy has a large positive deviation from Raoult's law, which implies a demixing tendency of silver in the Ag-Pt solid solution. Moreover, when temperature increases the silver activity in the alloy also increases which means the deviation from ideal is increasing with temperature. This activity dependence of temperature contradicts the general behavior of many common alloys. It means that the mixing entropy between two elements is abnormal which is also typical for arsenic, sulfur and zinc systems that are able to form stable intermetallic compounds [20]. The atomic size difference between two atoms may affect this deviation from ideality.

Between 573 and 673 K, the partial Gibbs energy of mixing of the solid Ag-Pt alloy containing 1 at % Ag can be expressed by equation (12),

$$\begin{aligned}\Delta_r\bar{G}_{Ag}\left(J\,mol^{-1}\right) &= -\left(12086 \pm 286\right) + \\ &+ \left(13.05 \pm 0.46\right)T\left(K\right) \qquad (12)\end{aligned}$$

From (Eq. 12) it can be obtained that the partial molar enthalpy ($\Delta\bar{H}_{Ag}$) and entropy ($\Delta\bar{S}_{Ag}$) of mixing of silver are –12086 J mol^{-1} and –13.05 J K^{-1}mol^{-1}, respectively. It can be seen that partial mixing entropy of silver in platinum is negative which means that at platinum rich side, silver tends not to mix with platinum. From this energetic point of view, it can be explained why the solubility of silver in the solid solutions of platinum rich alloys is very limited at low temperatures, as indicated by the Ag-Pt phase diagram.

5. Conclusion

Thermodynamic measurements of silver activity at different temperatures in a platinum-rich solid solution of Ag-Pt alloys containing 1 at % Ag have been executed. The microstructures of the homogeneous and heterogeneous phases and their compositions have been characterized by SEM and EPMA techniques. The partial molar Gibbs energy of silver dissolved in solid platinum can be obtained from the experimental data as

$$\begin{aligned}\Delta_r\bar{G}_{Ag}\left(J\,mol^{-1}\right) &= -\left(12086 \pm 286\right) + \\ &+ \left(13.05 \pm 0.46\right)T\left(K\right) \qquad (13)\end{aligned}$$

The results indicate that activity of silver in the Ag-Pt solid solutions has a strong positive deviation from Raoults' law.

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