Solubility of Palladium in Alumina-Iron Silicate Melts

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Dissolution and solubility of palladium in iron silicate melts saturated with alumina–iron spinel at 1300°C has been measured using an equilibration-drop quenching technique combined with electron probe microanalysis and laser ablation–inductive coupled plasma–mass spectrometry analysis from polished sections. Composition of the resulting Fe–Pd alloy allowed estimation of the activity of palladium at different oxygen partial pressures, and, thus, the solubilities of palladium in the studied slags in conditions typical of copper and nickel smelting as well as slag cleaning at $p_{O_2}=10^{-5}$ to 10^{-10} atm. The mechanism of palladium dissolution in the studied iron silicate slags was oxidation by formation of the monovalent oxide species $PdO_{0.5}$ over the entire oxygen activity range of this study. Testing the applicability of the various palladium isotopes for quantitative analyses of Pd in these types of matrices resulted in a good fit of measured concentrations of ^{104}Pd and ^{105}Pd with interference-corrected ^{106}Pd and ^{108}Pd .

INTRODUCTION

Palladium is one of the most important precious metals used in electrical and electronic equipment, as well as playing a critical role in catalytic converters. Palladium and platinum have similar properties, and thus, depending on their prices in metal exchanges, their use in the major application fields may change from platinum to palladium and back to platinum in a cyclical way. In general, palladium is a much less well-studied platinum group metal (PGM) in geochemical and metallurgical processes than platinum. Sullivan et al.¹ recently compiled the available solubility data for palladium in silicate melts as a function of oxygen partial pressure. They also summarized most of the earlier studies in geochemistry as a function of temperature and pressure.

Nishijima and Yamaguchi² determined PGM distributions between ternary Al_2O_3 – CaO – SiO_2 slags at copper saturation and 1450°C, measuring the oxygen activities with an EMF cell. Their distribution results were essentially independent of the $(CaO +$

$MgO)/(CaO + MgO + SiO_2)$ ratio (w/w). Shuva et al.³, Avarmaa et al.^{4,5} and Sukhomlinov et al.⁶ determined the distribution coefficients of palladium between selected secondary copper smelting slags and a copper alloy. Yamaguchi^{7,8} measured palladium distributions between copper and CaO – FeO_x slags at 1300°C and MgO saturation. Henao et al.⁹ carried out measurements on PGMs as trace elements in a copper matte–silicate slag system at MgO saturation at 1300°C. Avarmaa et al.¹⁰ and Piskunen et al.¹¹ studied palladium distributions in copper and nickel matte smelting conditions at silica saturation, and conducted direct phase composition measurements with laser ablation–inductive coupled plasma–mass spectrometry (LA-ICP-MS).

Tomiska¹² summarized the previous experimental data on the Fe–Pd system and carried out Knudsen cell measurements on ternary Au–Fe–Pd alloys. Ghosh et al.¹³ carried out a critical thermodynamic assessment of the Fe–Pd alloy system using the available thermodynamic and phase equilibrium information.

This study experimentally investigated palladium behavior in copper smelting and converting conditions (1300°C, $p_{O_2} = 10^{-10}$ – 10^{-5} atm) without the

presence of copper. The simultaneous presence of copper and palladium in LA-ICP-MS measurements is a demanding task, as copper argide ($^{65}\text{Cu}^{40}\text{Ar}^+$), potentially formed by the Ar ICP¹⁴ in copper-bearing systems, has almost the same molar mass as the ^{105}Pd isotope and they are therefore impossible to separate by a mass spectrometer running at low mass resolution. This problematic mass interference was a driver for the current measurements on Cu-free experiments, providing higher accuracy Pd distribution coefficient determinations with a pure palladium equilibrium phase instead of a dilute copper alloy^{4–6} or copper-bearing matte^{10,11}. Moreover, as PGMs are also recovered via metallic iron-slag systems,¹⁵ this study also provides valuable data and information for those technologies.

EXPERIMENTAL

The experimental technique involved sample equilibration at a controlled temperature, $1300 \pm 3^\circ\text{C}$, and in a flowing gas atmosphere, followed by rapid quenching and direct elemental analyses of the equilibrium phases with EPMA (electron probe microanalysis) and LA-ICP-MS from polished sections. The materials used in the experiments have been collected in Table S1 of the online Electronic Supplementary Material file. They were mixed and homogenized by grinding in an agate mortar with a metal alloy-to-slag ratio of 1:9 and a Fe/SiO₂ ratio of 1.3 (w/w) in slag. The CO-CO₂ gas mixtures used to generate the different oxygen partial pressures at 1300°C were controlled using thermal mass flow controllers (DFC 26; Aalborg, USA) of different flow ranges, with an accuracy of $\pm 1\%$ of full range. The gases were supplied by AGA-Linde (Finland) with purities of 99.97 vol.% CO and 99.9992 vol.% CO₂.

The details of the experimental furnace and the gas train have been described earlier.^{16,17} This study continues the PGM solubility studies in a similar Fe alloy–slag system with the same experimental arrangement and procedure as previously published for platinum.¹⁶ The sample and an alumina crucible as the sample holder in the hot zone of the experimental furnace are shown in Fig. 1(a). All the other experimental details, including the furnace, sample mass, equilibration time series, and analytical equipment, are available in the previous publication regarding platinum solubility in alumina–iron silicate slag.¹⁶ All the presented experiments were equilibrated for 48 h. A typical microstructure of the equilibrated-quenched sample is shown in Fig. 1(b).

SAMPLE CHARACTERIZATION

The elemental compositions of the quenched metal and slag were analyzed with EPMA, of which the analytical details have been presented earlier.¹⁶ The only change was that pure Pd was used as a standard for analyzing Pd L α peaks in the Pd-Fe alloy, as opposed to pure Pt for Pt L α . The averages of eight EPMA points have been reported as well as their standard deviations. The slag composition results are presented in more detail elsewhere.¹⁸

The slag and spinel phases were also analyzed by LA-ICP-MS, since the concentrations of palladium were below the detection limit of EPMA. The details of this equipment have also been presented earlier.¹⁶ For slag analysis, NIST 612 SRM¹⁹ was employed as the external standard and ^{29}Si as the internal standard. NIST 610, BHVO-20, and BCR-2G^{19,20} were analyzed as unknowns for monitoring the analysis accuracy. For spinels, GSD-1G²⁰ was chosen as the external standard and ^{57}Fe as the internal. The Pd concentration in GSD-1G was determined by analyzing this standard material as

Fig. 1. (a) Schematic of the hot-zone of the experimental furnace with the measuring thermocouple next to the sample. AL23 indicates ceramic DEGUSSIT AL23 (Al₂O₃) by Friatec (today Kyocera Fineceramics GmbH). (b) A typical microstructure of sample taken with SEM-BSE.

Table I. Re-analyzed palladium concentrations in slags for different isotopes

Sample	pO ₂ /atm	¹⁰⁴ Pd	¹⁰⁵ Pd	¹⁰⁶ Pd ^a	¹⁰⁸ Pd ^a
Pd8	10 ⁻⁵	70.4 ± 3.1	67.9 ± 1.8	58.9 ± 2.3	62.3 ± 2.2
Pd10	10 ⁻⁶	36.5 ± 2.5	34.0 ± 2.7	28.1 ± 1.5	31.3 ± 1.6
Pd6	10 ⁻⁷	16.8 ± 1.4	16.9 ± 0.8	16.4 ± 0.6	15.0 ± 0.7
Pd1	10 ⁻⁹	2.4 ± 0.3	2.1 ± 0.3	2.7 ± 0.3	2.6 ± 0.4
Pd3	10 ⁻¹⁰	0.8 ± 0.4	1.0 ± 0.2	0.9 ± 0.2	0.8 ± 0.2

^aValues achieved by using correction formulas^{4,23}.

Table II. The experimental data of this study by LA-ICP-MS (slag) and EPMA (alloy)

Sample	Log ₁₀ Po ₂	Slag	Pd-Fe alloy	
	atm	(Pd/ppmw)	(Pd/wt.%)	(Fe/wt.%)
Pd7	- 5.0	89.8 ± 1.2	95.56 ± 0.16	4.44 ± 0.06
Pd8	- 5.0	71.6 ± 1.7	96.48 ± 0.18	3.52 ± 0.10
Pd10	- 6.0	32.7 ± 1.7	92.43 ± 0.39	7.57 ± 0.16
Pd5	- 7.0	14.3 ± 0.2	90.63 ± 0.16	9.37 ± 0.05
Pd6	- 7.0	17.5 ± 0.2	90.50 ± 0.17	9.50 ± 0.06
Pd1	- 9.0	2.7 ± 0.1	81.76 ± 0.34	18.24 ± 0.08
Pd2	- 9.0	3.9 ± 0.3	83.90 ± 0.33	16.10 ± 0.10
Pd3	- 10.0	0.9 ± 0.1	78.81 ± 0.29	21.19 ± 0.11
Pd9	- 10.0	1.2 ± 0.1	75.91 ± 0.27	24.09 ± 0.16

an unknown, using NIST 612 as an external standard and ⁵⁷Fe as internal. The value obtained for Pd concentration was 33 ppm. The Glitter software package²¹ was applied for the raw data processing, i.e., the baseline reduction and quantifications.

The palladium concentrations were measured for all the existing isotopes ¹⁰⁴Pd, ¹⁰⁵Pd, ¹⁰⁶Pd, ¹⁰⁸Pd, and ¹¹⁰Pd by the LA-ICP-MS technique. In this study, due to the absence of copper in the experimental charges, the isotopes ¹⁰⁴Pd and ¹⁰⁵Pd provide interference-free measurements and could be used, as such, to present the final results. The interference caused by the formation of ⁸⁹Y¹⁶O⁺ for ¹⁰⁵Pd was evaluated negligible (< 2%) as the concentration of Y in NIST612 standard is only 38.3 ppmw (Y/Pd ratio = 36.5), and its influence was evaluated as 20% of the counts measured on ¹⁰⁵Pd when using high Y/Pd ratio (381.8) standard NIST610.²² The ¹⁰⁶Pd, ¹⁰⁸Pd, and ¹¹⁰Pd isotopes have isobaric interferences from Cd-isotopes when using NIST 612 SRM as the primary standard material and additionally ⁹⁴Zr¹⁶O⁺ for ¹¹⁰Pd.²³ Because Cd exists in the standards, but not in the experimental samples, the measured palladium results based on the ¹⁰⁶Pd and ¹⁰⁸Pd isotopes were lower than the true concentrations. Nevertheless, results for isotopes of ¹⁰⁶Pd and ¹⁰⁸Pd can be interference-corrected by using formulae presented

in the literature.^{4,24} Consequently, selected samples were re-analyzed for a range of Pd and Cd isotopes to allow correction of ¹⁰⁶Pd and ¹⁰⁸Pd and to verify the consistency of calculated Pd concentrations based on four different Pd isotopes (Table I).

As can be seen in Table I, palladium concentrations in slags based on different isotope measurements are internally consistent. This provides a good indication that the use of corrected ¹⁰⁶Pd and ¹⁰⁸Pd isotopes are applicable for systems when there are interference problems with the ¹⁰⁴Pd and ¹⁰⁵Pd isotopes, such as copper-containing slags (⁶⁵Cu⁴⁰Ar⁺) with the ¹⁰⁵Pd isotope.⁴ In this study, we employed the ¹⁰⁵Pd isotope results, as this isotope has a higher natural abundance, of 22.33%,²⁵ than ¹⁰⁴Pd (11%). The detection limits for the elements studied with EPMA and LA-ICP-MS obtained in this study have been summarized in Table S2 of the Electronic Supplementary Material file.

Only minor heterogeneities in some time-resolved MS spectra were observed in the samples, as indicated by the experimental uncertainties collected in Tables I and II. The time-resolved MS-signal profiles were generally smooth as a function of time, as indicated in Fig. 2; only occasional spikes were present. This indicates that only a few nanonuggets of palladium²⁶ were possibly present in the iron silicate slags prior to or after the quench.

Fig. 2. Time-resolved analysis signal profiles for palladium (^{105}Pd) of two LA-ICP-MS measurement points on slags equilibrated at 10^{-5} and 10^{-9} atm oxygen partial pressures and 1300°C ; the ablation started approximately at 20 s.

RESULTS AND DISCUSSION

The primary concentration data for palladium in the slag based on ^{105}Pd measurements are shown in Table II and Fig. 3 as a function of oxygen partial pressure. The vertical error bars show the experimental analytical standard deviations ($\pm 1\sigma$) calculated from the independent LA-ICP-MS analysis points of each sample, and the horizontal error bars for $\log_{10}p_{\text{O}_2}$ as a fixed value of ± 0.2 based on the full range accuracy of mass flow controllers and gas flow rates presented earlier.¹⁶ The re-analyzed sample results for ^{105}Pd (see Table I) fit well with the primary results measured and shown in Table II.

Due to the dissolution of iron during equilibration, the composition of the palladium alloy was strongly affected by the prevailing oxygen partial pressure of the system. The EPMA data of the solid alloy are shown in Table II and Fig. 4. Using these data, the solubility of palladium (i.e., in equilibrium with pure metal and excluding the effects of dissolved iron) in the slag can be evaluated using the relationship:

$$^*c(\text{Pd}) = c(\text{Pd})/a[\text{Pd}] \quad (1)$$

where $a[\text{Pd}]$ is the activity of palladium in the metallic Fe-Pd alloy,¹³ referred to pure solid palladium, and $c(\text{Pd})$ is the measured concentration of palladium in the slag at that activity. This corrected chemical solubility of palladium [$^*c(\text{Pd})$] in alumina spinel saturated iron silicate melt at 1300°C as a function of the oxygen partial pressure is presented in Fig. 5.

Figure 5 shows that the solubility of palladium in silicate melts at alumina–iron spinel saturation is strongly increasing as a function of the prevailing oxygen activity. Thus, over the entire oxygen partial pressure range studied, it was dissolved as an oxide species in the molten iron silicate melt.

Fig. 3. Concentration of palladium in alumina–iron spinel saturated iron silicate melts as a function of oxygen partial pressure at 1300°C , in equilibrium with solid iron–palladium alloy.

Selected experimental points were measured from the solid alumina–iron spinel phase and its palladium concentration in equilibrium with the molten slag. The spinel was essentially a binary solution of FeAl_2O_4 and Fe_3O_4 , as its silicon concentration at the studied oxygen partial pressure range was very low, between 0.035 and 0.055 wt.% (Si), equivalent to 0.075 and 0.12 wt.% SiO_2 . The obtained distribution coefficient of palladium between liquid slag (s) and solid spinel (sp), $L^{s/\text{spPd}} = (\text{wt.}\% \text{ Pd})_{\text{slag}} / (\text{wt.}\% \text{ Pd})_{\text{spinel}}$, shows a minor enrichment in the spinel at $p_{\text{O}_2} = 10^{-6} - 10^{-5}$ atm with $L^{s/\text{spPd}} = 0.45 \pm 0.2$.

The apparent distribution coefficient of palladium between the metal alloy and molten silicate has been defined conventionally²⁷ as:

$$L^{a/s}\text{Pd} = [\text{wt.}\% \text{ Pd}]_{\text{alloy}} / [\text{wt.}\% \text{ Pd}]_{\text{slag}} \quad (2)$$

where $[\text{Pd}]_{\text{alloy}}$ and $(\text{Pd})_{\text{slag}}$ are the concentrations of palladium in the corresponding phases. The functional relationship between L and the oxygen partial pressure can be obtained using the oxidic dissolution reaction of palladium in the slag, which can be written as:

where x refers to the oxidation degree of the palladium oxide present in the molten slag. The dissolving palladium in Eq. (3) was written as an alloy, due to dissolution of iron from the slag. Using the equilibrium constant equation of Eq. (3) combined with the apparent distribution coefficient $L^{a/s}\text{Pd}$ in Eq. (2), the reorganized form for the thermodynamic distribution coefficient ' $L^{a/s}\text{Pd}$ ' is:

Fig. 4. The measured (EPMA) iron concentration in the solid iron-palladium alloy as a function of the oxygen partial pressure at 1300°C.

Fig. 5. The chemical solubility of palladium in alumina spinel saturated iron silicate melt as a function of the oxygen partial pressure at 1300°C.

$$\begin{aligned} \log' L^{a/s} \text{Pd} &= \log L^{a/s} \text{Pd} + \log \{f[\text{Pd}]/n^T[\text{alloy}]\} \\ &= \log [1/K \cdot f(\text{PdO}_x)/n^T(\text{slag})] - x/2 \\ &\quad \cdot \log p_{\text{O}_2}. \end{aligned} \quad (4)$$

In this case, the composition of the palladium alloy, the activity coefficient of palladium $f[\text{Pd}]$, as well as the number of moles in the alloy, $n^T[\text{alloy}]$, vary so significantly that they must be taken into account when calculating the oxygen activity slope of the metal-slag distribution coefficient. In Eq. (4),

the symbols $n^T(\text{slag})$ and $n^T[\text{alloy}]$ refer to the number of moles in 100 g slag and alloy, respectively, K is the equilibrium constant of Eq. (3), and $f[\text{Pd}]$ and $f(\text{PdO}_x)$ are the Raoultian activity coefficients of palladium in the solid alloy and palladium oxide in the silicate melt, respectively. The obtained concentrations and activity data of palladium¹³ allowed us to estimate the dissolving oxide form of palladium in the slag according to the thermodynamic distribution coefficient derived in Eq. (4) and presented in Fig. 6. Additionally, the apparent distribution coefficient and reference studies are included in Fig. 6.

According to Eq. (4), the oxidation mechanism of palladium or the oxidation degree in the slag can be obtained from the slope of $\log' L^{a/s} \text{Pd}$ versus $\log p_{\text{O}_2}$ plot. The slope of the line was constant at 0.25 over the entire oxygen partial pressure range studied, as shown in Fig. 6. This suggests that the dissolving oxide species of palladium in the slag was $\text{PdO}_{0.5}$ or that palladium was present in the molten iron silicate as a monovalent cation Pd^+ . This agrees with our previous studies^{5,6} in the copper-slag system, where the palladium form in slags was evaluated to be $\text{PdO}_{0.5}$. Moreover, the observed oxidation mechanism of this study is in good agreement with the measurements of Borisov and Palme²⁸ and Laurenz et al.²⁹ Thus, no further discussion about the presence of Pd^0 at present oxygen partial pressures as delivered by Sullivan et al.¹ is necessary for iron-rich silicate slags. The relatively high palladium concentration (~ 100 ppm) found in the iron silicate slag at high oxygen partial pressures suggests reducing the slag cleaning conditions for successful palladium recovery. This may be related to the high stability of palladium oxide (standard Gibbs free energy of formation) at elevated temperatures.⁵ All the reference studies in Fig. 6 present distribution coefficients of palladium between copper and different slags, except for the geological study by Borisov and Palme.²⁸

Yamaguchi⁸ and Nishijama and Yamaguchi² reported copper-slag distribution coefficients for Pd which were approximately 1.5 orders of magnitude lower in logarithmic scale than the values obtained in the present study. The data by Shuva et al.³ at 1300°C suggested much higher palladium solubility in the slag and a strong influence of MgO concentration as well as of the slag basicity ($\text{CaO} + \text{MgO}/\text{SiO}_2$). The technique used in those studies was a bulk analysis by ICP-atomic emission spectroscopy of the slag where metal entrainment in sampling may cause major errors. Thus, in the cases of a high metal-to-slag distribution coefficient (> 100) the trace element concentrations in the slag can be seriously distorted. In the above cases,^{2,3,8} the distribution coefficients reported were 1.5–2 orders of magnitude in log scale smaller than obtained in this study, where true chemically

Fig. 6. The thermodynamic distribution coefficient of palladium between pure metallic Pd and molten iron silicate slag saturated with solid alumina-iron spinel at 1300°C. The apparent distribution coefficient values obtained in this study, as well as results of several earlier studies, have been plotted for comparison.

dissolved concentrations were measured by direct phase analyses of the glassy silicate phase without the need for mechanical phase separation.

The distribution coefficients of Pd between copper and iron silicate slag at 1300°C by Avarmaa et al.⁵ and Sukhomlinov et al.⁶ are slightly higher than the ones obtained in this study. The values obtained by Avarmaa et al. between copper and high-alumina iron silicate slag⁴ correspond to the present values in reducing conditions but are also slightly on the higher side in oxidizing atmospheres. A comparison of the present experimental solubilities of palladium with geochemical data from low-iron basaltic silicates at 1300–1350°C and 1 atm total pressure by Sullivan et al.¹ and Borisov and Palme²⁸ are in good agreement with the values obtained in this study at 1300°C. The distribution coefficients of Pd between pure Pd ($\alpha = 1$) and basalts were slightly on the higher side in oxidizing conditions but similar to our results in reducing conditions.^{1,28}

The influence of copper on the distribution coefficient of palladium has been small when compared to our previous studies^{4–6} in copper-saturated systems, as the distribution coefficients obtained previously were of the same order of magnitude despite the presence of metallic copper, especially in the reducing conditions. Additionally, this study clarifies the behavior of palladium at reducing, low-oxygen partial pressure conditions, in which the concentrations in slags at copper saturation were previously below the detection limits of LA-ICP-MS.^{4,6} Here, we have also provided strong evidence that with $\text{FeO}_x\text{-SiO}_2\text{-Al}_2\text{O}_3$ slags containing copper, palladium results can be presented according to concentration results achieved with isotope ^{104}Pd or with corrected results by isotopes ^{106}Pd and ^{108}Pd . Nevertheless, when new systems containing

additional elements are characterized with LA-ICP-MS, all possible isobaric interferences need to be considered and carefully examined.

CONCLUSION

Palladium is a critical element of the EU, the availability of which in the future needs to be secured. This study provided new insights to its behavior, recyclability, and recoverability via ferrous and non-ferrous smelting conditions. In order to confirm the solubility of palladium in alumina-rich iron silicate slags, an experimental series was completed with direct contact between palladium and the slag. The experimental conditions were typical copper and nickel smelting/converting as well as slag cleaning conditions at $p_{\text{O}_2} = 10^{-5}$ to 10^{-10} atm and 1300°C. The obtained results formed a coherent dataset with a constant thermodynamic distribution coefficient versus the p_{O_2} slope of 0.25, indicating a solution of Pd as the $\text{PdO}_{0.5}$ (Pd^+) form in slag, for the metal-slag distribution coefficient between 10^4 and $10^{5.5}$.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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SUPPLEMENTARY INFORMATION

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