Failure mechanisms in Pt-Rh_x thermocouple sensors caused by gaseous phosphorous species

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Abstract

Interactions between Pt-Rh sensor alloys and P-containing gas in an environment simulating a carbon feedstock gasification process were investigated. A series of exposure tests revealed materials failure through two distinct P diffusion mechanisms, depending on Rh concentrations; intergranular diffusion in low Rh alloys and intragranular diffusion in high Rh alloys. Upon exposure, P rapidly migrated into the alloys, lowering the melting temperature of the alloys and/or forming intermediate phases with Rh at grain boundaries or within grains. The failure mechanisms of Pt-Rh alloys by P-bearing gas in the conditions studied are proposed.

Keywords:

A. Platinum

B. SEM

B. XRD

C. High temperature corrosion

C. Intergranular corrosion

C. Thermodynamic diagrams

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1. Introduction

Platinum (Pt) and alloys of it are used for high temperature applications; including sensors, crucibles, catalysts, etc.; because they have superior resistance to corrosion by common acids and alkalis and because they have good oxidation resistance at high temperatures [1]. In sensor applications such as thermocouples used at high temperatures, Pt is usually alloyed with rhodium (Rh) at different concentrations (0 – 30 wt.%) to induce a voltage difference corresponding to the temperature being measured. For example, a type B thermocouple, which is considered reliable for temperature measurements up to 1700 °C, consists of two Pt alloys; one containing 30 wt.% Rh, the other with 6 wt.% Rh [2]. While Pt is considered to be relatively inert, Pt based sensors often suffer failure in severe industrial environments because of phase de-stabilization caused by interactions with certain gaseous species.

Integrated Gasification Combined Cycle (IGCC) gasifiers are used to generate electric power and/or chemicals from carbon feedstock such as coal and petcoke [3] and involve high temperature, pressure, corrosive gases, and slags. In the U.S., coal is a common feedstock for gasification, typically containing 5 – 20 wt.% ash constituents [4], some of which can be volatile (K_2O , Na_2O , P_2O_5 , and SO_3) [5]. IGCC gasifier conditions ($P_{O_2} = 10^{-9} - 10^{-7}$ atm and 1325 – 1575 °C) [6] promote the evolution of gaseous species with these volatile constituents, some of which are known to cause hot corrosion or fouling issues in downstream parts of the gasifier [7]. Volatilized P and S are known to poison Pt based sensors and catalysts, leading to materials failure [1, 8].

Although S poisoning of Pt alloys has been extensively studied in the literature [8-12], only a few technical papers have discussed the effect of P on Pt alloys [13, 14]. Mundschau and Vanselow [13] studied the P adsorption on Pt surfaces using the field emission electron microscope (FEM). Ma et.al [14] analyzed CO diffusion on a P-contaminated Pt (111) surface. A mechanism explaining how P interacts with Pt based alloys and an assessment of material interactions has not been reported in the literature. In the present work, P interactions with Pt-Rh alloys were experimentally investigated. A mechanism of Pt-Rh alloy deterioration by P attack under gasification conditions is discussed.

2. Experimental

In this research, the failure of type B thermocouples (94 wt.% Pt-6 wt.% Rh/70 wt.% Pt and 30 wt.% Rh) caused by gaseous phosphorous was analyzed in two atmospheres: CO and 64 vol.% CO-36 vol.% CO_2 (hereafter shown as CO/ CO_2). Oxygen partial pressures in the carbon gas mixtures at fixed CO/ CO_2 ratios are not thermally constant but change with temperature. The thermodynamic computation software, FactSage 6.4 (with the FactPS database) [15] indicates: the partial pressure of oxygen in the CO gas increases from negligible at 25 °C to 10^{-19} atm at 1000 °C; and in the CO/ CO_2 , it changes from negligible at 25 °C to 10^{-15} atm at 1000 °C. Gases

(99.5 wt.% purity CO and 99.99 wt.% purity CO₂) used to produce specific partial pressures of oxygen were manufactured by Matheson (USA).

Reagent grade aluminum phosphate powder of 99.6% purity (40.6 wt.% Al₂O₃ and 59.0 wt.% P₂O₅) and < 5 μm size (Alfa Aesar - USA), was used as the source of gaseous P. X-ray diffraction analysis (XRD, Rigaku Ultima IV XRD spectrometer (Cu Ka, 40 kV, 40 mA)) using MDI Jade 9 XRD analysis software [16] indicated the aluminum phosphate sample consisted of approximately 92.4 wt.% AlPO₄, 7.2 wt.% AlP₃O₉ and 0.4 wt.% Al₂O₃. The 94 wt.% Pt-6 wt.% Rh (Pt-6Rh hereafter) and 70 wt.% Pt-30 wt.% Rh (Pt-30Rh hereafter) wires of 0.4 mm diameter manufactured by Engelhard (USA) were oxyacetylene welded at the location where the two wires were joined to build a type B thermocouple. The experimental set-up used for exposing thermocouple assemblies to the test environment is shown in Fig. 1. These Pt-Rh wires were placed into protection alumina tubing (3 mm ID) with the welded tip exposed directly to a P-bearing gas inside the alumina reaction tube.

Fig. 1. Experimental set-up used in the present work.

For all tests, 2.8 g of aluminum phosphate powder was placed in a 99.9 wt.% alumina crucible (26 mm H × 22 mm OD, 18 mm ID) with a similar composition alumina lid as a cover (Fig. 1). A type B thermocouple sample was positioned in a way that the exposed tip was just above the aluminum phosphate powder without physical contact. During testing, the electromotive force (EMF) output of the thermocouple assembly was continuously recorded by measuring the voltage potential. Two openings (each 4×4 mm) were added on the gas inlet and outlet sides of the crucible to promote gas movement through the crucible. The type B thermocouple and the crucible with the aluminum phosphate powder were set on an alumina boat in the hot zone of a horizontal CM Rapid Temp 1800 Furnace (USA). Heating and cooling rates during experiments were programmed and controlled using a programmable temperature controller. Sample temperature changes were continuously recorded by the thermocouple itself via its EMF while the cooling rate after sensor failure was assumed to follow the programmed temperature profile. The furnace was purged with designated gases (CO or a CO/CO₂ gas mixture) at 30 ml/min throughout the test.

Experimental conditions used to evaluate interactions and reactions among Pt, Rh, and P are summarized in Table 1. In the 1st part of the study (Table 1, 1st set), a thermocouple sensor was heated in a CO gas environment to 1500 °C at 150 °C/hour, then cooled to room temperature at the same rate to investigate the temporal and thermal occurrence of wire failure. The experiment was repeated for the CO/CO₂ gas mixture.

In the 2nd part of the study (Table 1, 2nd set), a thermocouple sensor was heated in a CO gas environment at the same heating rate used for the 1st part (150 °C/hour), but quenched in clean water at room temperature immediately after failure of the thermocouple was noted (EMS output from the sensor assembly discontinued). Prior to quenching, the reaction tube was purged with Ar (99.999% purity) at 100 ml/min for 20 min, then the sample was quickly removed and quenched in water. The total time from opening the furnace to quenching in water was less than 30 seconds. This part of the experiment was repeated for the CO/CO₂ gas environment.

The 3rd part of the study used the same experimental technique as for the 1st and 2nd sets. Two pairs of thermocouple wires (Table 1, 3rd set) on an alumina support were independently exposed to the CO gas environment in the presence of aluminum phosphate. One of the two pairs was heated to 950 °C at 150 °C/hour, followed by water quench, while the other pair was heated to 1500 °C at 150 °C/hour, followed by furnace cooling to room temperature at 150 °C/hour. The temperature (950 °C) was assumed to be near the thermocouple failure temperature determined from the 1st and 2nd experiments. Samples of the 3rd part of the study were analyzed by XRD for crystalline phase changes. Sensor wires were folded into a spiral shape of 9 mm diameter prior to controlled atmosphere testing to maximize the surface area density required for XRD analysis.

Table 1. Experimental conditions used in this work.

Experiment	Target temp. (°C)	Heating rate (°C/hour)	Gas environment	Materials studied	Comments
1 st set	1500	150	CO; CO/CO ₂	Welded type B thermocouple	Heated to 1500 °C and cooled at 150 °C/hour to room temperature
2 nd set	1500	150	CO; CO/CO ₂	Welded type B thermocouple	Heated toward 1500 °C and water quenched at failure
3 rd set	950	150	CO	Separate wires of Pt-6Rh, Pt-30Rh	Heated to 950 °C and water quenched
	1500	150	CO	Separate wires of Pt-6Rh, Pt-30Rh	Heated to 1500 °C and cooled at 150 °C/hour to room temperature

All exposed samples were analyzed for phase changes using optical microscopy and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS, FEI Inspect F and an Oxford INCA WAVE spectrometer).

3. Results

Voltage readings from the thermocouple samples exposed to the P-enriched CO and CO/CO₂ environments were converted to temperature and are shown in Fig. 2.

Fig. 2. Type B thermocouple temperature readings caused by exposure to: (a) P-rich CO environment, heated to 1500 °C and cooled to room temperature; (b) P-rich CO/CO₂ environment, heated to 1500 °C and cooled to room temperature; (c) water quenched at sensor failure during heating in the P-rich CO environment; and (d) water quenched at sensor failure during heating in the P-rich CO/CO₂ environment.

On heating, thermocouple readings from the experiment conducted in the CO environment indicate failure at 929 °C, with irregular fluctuation above that temperature (Fig. 2(a)). Such a discontinuity in sensor readings is observed at 950 °C for the CO/CO₂ environment (Fig. 2(b)). The discontinuity in the EMF output generally indicates local chemistry damage and/or an open thermocouple. To investigate the cause of the discontinuity in thermocouple output, the 2nd set of thermocouple samples was quenched in water immediately after the EMF discontinuity occurred to freeze in the failed microstructure. The recorded data from the 2nd set indicate a discontinuity at 948 °C for the sample treated in the CO and 979 °C for the sample treated in the CO/CO₂ (Fig. 2(c and d)). In both sets, the discontinuity in readings from the CO environment occurs at a lower temperature than that from the CO/CO₂ environment exposure. The difference in failure temperature (for the same gas environment) between the 1st set and the 2nd set would be attributed to a combination of multiple factors including a subtle variation in thermocouple location above the aluminum phosphate powder and slight differences in sample interactions with the gaseous environment.

As a reference, data readings from a thermocouple sample exposed to the CO/CO₂ gas mixture without aluminum phosphate are shown in Fig. 3. Any irregularity or discontinuity throughout the experiment is not noted while heating to 1500 °C at 150 °C/hour, holding for 3 hours at that temperature, and cooling to room temperature at the same rate.

Fig. 3. Type B thermocouple temperature readings in the CO/CO₂ gas mixture without aluminum phosphate.

3.1. Optical and SEM-EDS results of slow cooled samples (1st set, Table 1)

The thermocouple wires from the 1st set are found melted and shaped into spheres. Some portions partly melted and remained in the alumina protection tubing as shown in Fig. 4(a and b). The most severe melting is observed for sensor wires exposed to the CO environment (Fig. 4(a)) versus wires exposed to the CO/CO₂ atmosphere (Fig. 4(b)).

Fig. 4. Cross-sectional optical images of the thermocouple wires heated to 1500 °C and cooled to room temperature in alumina tubes treated: (a) in CO; and (b) in CO/CO₂. Note spheres shown in (b) are not cross-section.

SEM-EDS analysis of the cross-sectioned sensor wires is summarized in Table 2. Thermocouple wires treated in the CO formed two solid phases (Table 2) in the Rh deficient Pt-matrix enriched with P (Fig. 5(a and b)). The averaged Pt-matrix compositions of the sample exposed to CO with

aluminum phosphate present is 89.60 at.% Pt-0.90 at.% Rh-9.50 at.% P for the Pt-6Rh and 84.96 at.% Pt-0.48 at.% Rh- 14.56 at.% P for the Pt-30Rh. In the CO/CO₂ environment with aluminum phosphate present, the formation of the Pt-Rh-P compound is found in the Rh deficient Pt-matrix (averaged composition: 97.26 at.% Pt-2.74 at.% Rh for the Pt-6Rh and 84.01 at.% Pt-15.99 at.% Rh for the Pt-30Rh) (Fig. 5(c and d)). Two distinguishable solid phases formed in the Pt-matrix. The averaged elemental composition of the first phase (PRh₂) is found to be 13.56 at.% Pt-53.93 at.% Rh-32.64 at.% P (Table 2). The second phase (P₂Pt) is predominately P and Pt with negligible Rh present (averaged composition: 33.37 at.% Pt-0.14 at.% Rh-66.50 at.% P, Table 2). Formation morphology of these solid phases varied under different conditions. Phases formed in the Pt-6Rh wire in the CO are more angular while those formed in the other conditions are roundish. All the wires exposed to the CO environment and all the wires with 30 wt.% Rh exhibit more solid precipitation of the Pt-Rh-P phases.

Fig. 5. SEM backscattered electron images of the cross-sectioned thermocouple wires heated to 1500 °C and cooled to room temperature: (a) Pt-6Rh treated in CO; (b) Pt-6Rh treated in CO/CO₂; (c) Pt-30Rh treated in CO; (d) Pt-30Rh treated in CO/CO₂. PRh₂ and P₂Pt chemistry is shown in Table 2. Matrix in (a) and (b) is Rh poor Pt enriched with P, and that in (c) and (d) is Rh deficient Pt.

Table 2. Averaged SEM-EDS elemental analysis of the solid phases formed in the Pt-Rh_x wires (at.%).

Phase	Exp.	Alloy compositions	Gas environment (with AlPO ₄ present)	Pt (at.%)	Standard deviation	Rh (at.%)	Standard deviation	P (at.%)	Standard deviation	Total (at.%)	Element ratio
(Pt+Rh)/P											
PRh ₂ (slow cooled wires from 1500 °C)	1 st set	Pt-6Rh	CO/CO ₂	11.76	0.8	56.00	0.8	32.24	0.4	100	2.1
	1 st set	Pt-30Rh	CO/CO ₂	7.52	0.9	59.60	0.8	32.88	0.4	100	2.0
	1 st set	Pt-6Rh	CO	13.51	2.8	54.45	2.5	32.04	0.4	100	2.1
	1 st set	Pt-30Rh	CO	15.11	0.8	52.99	0.9	31.90	0.5	100	2.1
	3 rd set	Pt-6Rh*	CO	16.80	0.1	50.65	0.2	32.55	0.1	100	2.1
	3 rd set	Pt-30Rh*	CO	16.66	1.1	49.89	1.9	33.45	1.0	100	2.0
	Average			13.56		53.93		32.51			2.1
P/(Pt+Rh)											
P ₂ Pt (slow cooled wires from 1500 °C)	1 st set	Pt-6Rh	CO	33.11	0.5	0.21	0.3	66.68	0.3	100	2.0
	1 st set	Pt-30Rh	CO	33.34	0.4	0.20	0.3	66.46	0.3	100	2.0
	3 rd set	Pt-6Rh*	CO	33.25	0.2	0.13	0.2	66.62	0.1	100	2.0
	3 rd set	Pt-30Rh*	CO	33.77	0.4	0.00	0.0	66.23	0.4	100	2.0
	Average			33.37		0.14		66.50			2.0
(Pt+Rh)/P											
PRh ₂ (water quenched wires)	2 nd set	Pt-6Rh	CO/CO ₂	9.85	0.5	58.06	0.4	32.09	0.1	100	2.1
	2 nd set	Pt-30Rh	CO/CO ₂	8.87	0.7	58.48	0.7	32.65	0.3	100	2.1
	2 nd set	Pt-6Rh	CO	10.49	0.2	57.04	0.2	32.46	0.2	100	2.1
	2 nd set	Pt-30Rh	CO	10.74	0.2	56.62	0.3	32.65	0.4	100	2.1
	3 rd set	Pt-6Rh*	CO	13.96	0.6	53.45	0.7	32.59	0.6	100	2.1
	3 rd set	Pt-30Rh*	CO	11.03	0.4	55.57	0.3	33.40	0.5	100	2.0
	Average			10.82		56.54		32.64			2.1

* Samples used for the XRD analyzes.

Each point presented in Table 2 is an average of 4+ measurements, with the total number of measurements exceeding 100.

3.2. Optical and SEM results of quenched samples (2nd set, Table 1)

Optical images of the quenched type B thermocouples exposed to the P-enriched CO and CO/CO₂ environments are presented in Fig. 6. All thermocouple junction tips are severely attacked by P, causing thermocouple sensor failure.

The thermocouple sensor wires exposed to the CO environment seemed to experience greater interactions with P (Fig. 6(a and c)) than the wires exposed to the CO/CO₂ gas environment (Fig. 6(b and d)). Grain boundaries of the wires are more severely attacked by P in the samples with a low Rh content (6 wt.% Rh). The right portion of the wire in Fig. 6 is minimally affected by corrosive P as it was covered in an alumina protective tube.

Fig. 6. Optical images of the longitudinally cross-sectioned thermocouple wires of: (a) Pt-6Rh in CO; (b) Pt-6Rh in CO/CO₂; (c) Pt-30Rh in CO; and (d) Pt-30Rh in CO/CO₂, quenched at failure during heating.

Fig. 7 shows SEM backscattered electron micrographs of cross-sectioned thermocouple samples after the heat treatment. In the Pt-6Rh wire, P in grain boundaries leads to grain boundary melting and the formation of the Pt-Rh compound (Fig. 7(a and b)). The Pt-30Rh wires, on the other hand, experiences melting of the outer surfaces dominated by P-containing phases, while the original alloy matrix inside the protection tube is intact during the heat treatment conducted in this work (Fig. 7(c and d)). This supports the contention that sensor wire interactions with phosphorous was by vapor phase, which occurred first on the surface of the sample.

The presence of the PRh₂ phase (dark phase in Fig. 7) is noted in all the quenched thermocouple wires. The SEM-EDS elemental analysis of the PRh₂ phase is shown in Table 2. Note a greater fraction of the PRh₂ phase is observed in the wires treated in the CO gas environment than those treated in the CO/CO₂ (Fig. 7(a and c)). Morphology of the PRh₂ phase formed in wires with a higher Rh content (30 wt.%) varies depending on radial location, with it being blocky in the outer melted layers and lamellar-like in the lattice near the liquid/Pt-grain interface (Fig. 7(c and d)). Note the PRh₂ phase is only found in the grain boundaries for thermocouple wires with a low Rh content (6 wt.%). All the wires in the 2nd set of the experiment, except the Pt-30Rh wire treated in the CO, show the presence of layers at the molten outer surface. A melted layer is also found in the quenched thermocouple wires of the 3rd set of experiment prepared for the XRD.

A needle-like phase is present in the melted layers of quenched samples (not found in the slow cooled samples heated to a higher temperature). The phase was not conclusively identified using MDI Jade 9 and its XRD databases (ICDD 2015). EDS point analysis shows constant chemistry of the needle-like phase – averaging 53.30 at.% Pt-28.16 at% Rh-18.54 at.% P. From the

chemistry, it may not be an extension from any of the three binary systems, but may be a true ternary phase which has not been reported in the literature. Chemistry of the needle-like phase is independent of existing binary intermediate phases and the melted layer. Determination of the exact chemistry with SEM is limited due to small sizes. From its morphology, this phase was likely not present before quenching, but may have metastably formed at the present quenching rate. Further investigation of this phase is underway.

Fig. 7. SEM backscattered electron images of the longitudinally cross-sectioned thermocouple wires of: (a) Pt-6Rh in CO; (b) Pt-6Rh in CO/CO₂; (c) Pt-30Rh in CO; and (d) Pt-30Rh in CO/CO₂, quenched at failure during heating. PRh₂ chemistry is given in Table 2.

3.3. XRD results (3rd set, Table 1)

The XRD patterns of the cross-sectioned samples quenched from 950 °C and those slow heated to and cooled from 1500 °C in the P-rich CO environment are presented in Fig. 8.

Fig. 8. XRD patterns of the cross-sectioned samples treated in the P-rich CO environment: (a) Pt–6Rh wire quenched at 950 °C; (b) Pt–30Rh wire quenched at 950 °C; (c) Pt–6Rh wire slow heated/cooled from 1500 °C; and (d) Pt–30Rh wire slow heated/cooled from 1500 °C.

XRD analysis shows the presence of the PRh_2 phase in all the quenched wires (Fig. 8(a and b)). The PRh_2 peak locations are slightly shifted to the left (i.e., toward lower 2 theta) due to Pt incorporation (~13 at.%, Table 2) with respect to the pure PRh_2 standard with no Pt. The Pt peaks of the treated Pt-30Rh wire exhibit clear splits (Fig. 8(b)), indicating the presence of two Pt-Rh solid solutions with a variation in Rh content: 1) Rh-deficient Pt (1_a); and 2) remaining Pt-30Rh grains (1_b). Compositions of the Pt-Rh solution and the remaining grains are similar in the Pt-6Rh, with almost identical XRD patterns (Fig. 8(a)). As a result, peak splits for the Pt-6Rh wire are not as apparent as those in Fig. 8(b). In the slow heated/cooled sample, two intermediate phases, PRh_2 and P_2Pt , are noted (Fig. 8(c and d)). PRh_2 peaks are found shifted to the left as a result of ~17 at.% Pt incorporation in the phase (Table 2). Unidentified peaks in XRD patterns of the quenched samples are likely related to the needle-like phase found in the melted layers.

4. Discussion

In the earlier work by the present authors [17], the phosphorous movement inside an AlPO_4 -containing gasifier refractory was reported to occur via vapor phase transport, following the breakdown: $4\text{AlPO}_4(\text{s}) = 2\text{Al}_2\text{O}_3(\text{s}) + 2\text{O}_2(\text{g}) + (\text{P}_2\text{O}_3)_2(\text{g})$. A similar breakdown is expected for

AlP_3O_9 (metaphosphate): $\text{AlP}_3\text{O}_9(\text{s}) = \text{AlPO}_4(\text{s}) + \text{P}_2\text{O}_5(\text{g})$, where P_2O_5 gas may be produced instead of $(\text{P}_2\text{O}_3)_2$ at 700 °C (atmosphere was not reported) [18]. Decomposition of phosphates producing the gas phases $(\text{P}_2\text{O}_3)_2$ or P_2O_5 is impacted by both temperature and oxygen partial pressure – increasing with temperature or decreasing with oxygen partial pressure [19]. Phosphorous gas released may interact with the thermocouple installed within the gasifier refractory lining, causing sensor materials failure.

4.1. Thermodynamic aspect

The aluminum phosphate used in the study contained approximately 7 wt.% of AlP_3O_9 (s), which was experimentally reported to break down at 700 °C [18], causing a rapid increase in the vapor pressure of P_2O_5 above 700 °C on heating. The equilibrium decomposition temperature would be thermodynamically lower in carbon gas environments. FactSage calculations indicate the presence of the $(\text{P}_2\text{O}_3)_2$ gas in a low partial pressure of oxygen. In the present samples, as AlP_3O_9 was heated in reducing atmospheres induced by CO and CO_2 , more P-bearing vapor with $(\text{P}_2\text{O}_3)_2$ being the primary P-containing species was generated in the gas phase. In the CO environment, the partial pressure of oxygen was lower compared to that in CO/CO_2 , which promoted more generation of $(\text{P}_2\text{O}_3)_2$. Assuming thermocouple reading discontinuity reflects material failure during heating, the failures occurs in the temperature range of 929 – 979 °C. This indicates that the Pt-Rh alloy samples were attacked by the P-bearing gas above the decomposition temperature reported for AlP_3O_9 .

As P diffused into a sample, a concentration gradient is created establishing new phase equilibria across the wire, corresponding to a diffusion profile. For the quenched Pt-6Rh and Pt-30Rh wires, phase equilibria in the ternary Pt-Rh-P system were analyzed (Fig. 9(a and b)). Equilibrium tie-lines (global and/or metastable) must exist between a crystalline phase formed and a matrix such as grain boundaries and grains where the crystal precipitated out. PRh_2 is considered to be at equilibrium with the Pt matrix because of their coexistence. Original wire compositions are marked on the diagrams as solid circles. As can be seen from the Fig. 9(a and b), compositions of the PRh_2 particles are consistent for 6 wt.% Rh and 30 wt.% Rh samples in both environments (CO and CO/CO_2). A higher Rh content is found in the Pt matrix of wires treated in the CO/CO_2 gas environment than in the CO . In the CO gas environment, more P-bearing gas is likely produced and interacted with Pt-Rh alloys, removing more Rh from the matrix to form PRh_2 . As a result, the remaining matrix became lower in Rh.

EDS area scans of the melted layer are also plotted on the ternary diagram (Fig. 9). The needle-like phase is included in the area scans to determine the original liquid chemistry at the designated temperature as the phase was not likely present before quenching.

By assuming Pt and Rh atoms are substitutional and share the same crystallographic sites in PRh_2 for Pt incorporation, the $(\text{Pt} + \text{Rh})/\text{P}$ atomic ratio of the PRh_2 phase would be equivalent to the Rh/P ratio of the PRh_2 phase in the binary Rh-P phase diagram [20]. The $(\text{Pt} + \text{Rh})/\text{P}$ atomic

ratio of the PRh_2 phase formed is 2.1 (average, Table 2), which is similar to the theoretical value of the binary PRh_2 phase ($\text{Rh}/\text{P} = 2.0$) (Fig. 10(a)). The PRh_2 present is therefore determined to be a ternary extension of the binary PRh_2 phase with approximately 11 at.% Pt. The phase identification is confirmed by XRD analysis (Fig. 8).

The slow cooled sensor wires treated in the CO formed another crystalline phase, P_2Pt , as shown in Table 2, containing almost no Rh. Assuming Pt and Rh share the same crystallographic site, the $\text{P}/(\text{Pt} + \text{Rh})$ elemental ratio of this phase is determined to be similar to the theoretical P/Pt ratio of the binary P_2Pt phase, as indicated in the binary Pt-P phase diagram [21] in Fig. 10(b). XRD analysis of the slow cooled samples confirms the presence of P_2Pt in the wires (Fig. 8). In the binary phase diagram [21], P_2Pt is shown as a stoichiometric compound stable up to above 1500 °C. Note P_2Pt is not found in the quenched wires. This phase likely formed above 1000 °C on slow cooling from 1500 °C to room temperature.

Fig. 9. Phase compositions for the quenched Pt-Rh wires exposed in P-bearing gases: (a) Pt-6Rh in CO and CO/CO₂; and (b) Pt-30Rh in CO and CO/CO₂. Lines indicate equilibrium tie lines between PRh_2 and the matrix.

Fig. 10. Binary phase diagrams of: (a) P-Rh [20]; and (b) P-Pt [21]. Arrows indicate chemistries of PRh_2 and P_2Pt determined from elemental ratios of Pt, Rh, and P assuming substitutional solutions (Table 2).

4.2. Mechanisms of the Pt-Rh alloy failure by P-bearing gas

As temperature rises in the test environment, more P_2O_5 and/or $(\text{P}_2\text{O}_3)_2$ gas would be generated through AlP_3O_9 decomposition in the present atmospheres, according to FactSage calculations (with $(\text{P}_2\text{O}_3)_2$ being predominant). The formation of the PRh_2 compound within the sample indicates that dissociation of the P_2O_5 and/or $(\text{P}_2\text{O}_3)_2$ gas was necessary to take place at the gas-solid interface for P atoms to diffuse into the Pt-Rh wire.

In the present work, two distinct materials failure mechanisms driven by P diffusion into the Pt-Rh alloys are identified, depending on Rh content. In the Pt alloy with low Rh content (6 wt.%), intergranular diffusion is dominant, while intragranular diffusion is governing the P mass transport into the Pt alloys with high Rh content (30 wt.%). Each diffusion mechanism creates a unique structural degradation, ultimately leading to sensor material failure.

In the first case with low Rh content (Pt-6Rh), material failure is caused primarily by intergranular diffusion of P into the Pt-Rh alloy. P exhibits a higher chemical affinity for Rh to form intermediate phases than to Pt. This is experimentally evidenced by the presence of the P-Rh based intermediate phase while no P-Pt based intermediate phase is observed in samples. With the low Rh content, grain boundary diffusion is favored over the lattice diffusion due to the insufficient chemical driving force established by local equilibrium at the gas/lattice interface. An Rh concentration drop in the lattice near the grain boundary implies that Rh diffuses from the fcc-Pt lattice to the grain boundaries. At higher temperature, P diffuses more rapidly through grain boundaries where it reacts with Rh to form PRh_2 . As more P is transported with time, PRh_2

coalesces and grows in the grain boundaries (Fig. 11(a and b)). The remaining Rh-deficient Pt stays in the surrounding matrix and is continuously fed with incoming P, which locally lowers the liquidus temperature causing the grain boundaries to melt. As a result, the grain boundaries are widened as more material is consumed from the lattice. The remaining Pt-Rh grains in Fig. 11(a) are found to contain ~ 3 wt.% Rh, with no P indicating the Rh loss is caused by Rh diffusion from the grains to the grain boundaries. A melted layer of the P-saturated and Rh-deficient Pt is found in the affected grain boundary zones. EDS area scans of the melted layer (including the needle-like phase) marked in Fig. 11(a) indicate 12.51 at.% P, 11.57 at.% Rh, and 75.82 at.% Pt. Grains with voids near the interface with the melted layer are present, which likely formed through the Rh-driven Kirkendall effect [22]. A thin liquid layer with large PRh_2 precipitates formed at the outermost surface due to high P and Rh concentrations at the gas/alloy interface.

Fig. 11. SEM backscatter images of the cross-sectioned thermocouple wires: (a) Pt-6Rh in CO; and (b) Pt-6Rh in CO/CO₂, quenched at failure during heating. EDS area scans of the melted layer (including the needle-like phase) indicates 12.51 at.% P, 11.57 at.% Rh, and 75.82 at.% Pt.

In the second case with the high Rh content (Pt-30Rh), the failure of the Pt-Rh alloy is initiated by intragranular diffusion of P into the lattice. The strong chemical affinity of Rh for P is facilitated through the relatively large driving force induced by the local equilibrium established at the gas/alloy interface because of the high Rh concentration in the Pt alloy. The majority of P diffuses into the grains and reacts with Rh to form PRh_2 in the lattice. Further P enrichment facilitates the growth of PRh_2 and melting of the remaining Rh-poor and P-rich matrix. The size of PRh_2 is found to be larger toward the gas/metal interface (across the P concentration gradient). As more P diffusion progresses, a local system crosses the original equilibrium tie-line into a 'new phase' region; one where PRh_2 is in equilibrium with liquid other than with fcc-Pt (Fig. 9(b)). Note the presence of the two-phase regions across the concentration gradient is produced due to the non-isothermal nature of the experiment.

In the case with the high Rh content, the reaction layer can be separated into 3 zones across the P concentration gradient (Fig. 12(a and b)):

Zone 1. The initial PRh_2 formation in the Pt-Rh lattice

Zone 2. Liquid coexisting with PRh_2

Zone 3. The outmost melted layer of Rh-deficient Pt saturated with P

Fig. 12. SEM backscatter images of the cross-sectioned thermocouple wires: (a) Pt-30Rh in CO; and (b) Pt-30Rh in CO/CO₂, quenched at failure during heating. Zone 1: the initial PRh_2 formation in the Pt-Rh lattice. Zone 2: liquid coexisting with PRh_2 . Zone 3: the outmost melted layer of Pt saturated with P. EDS area scans of the melted layer (including the needle-like phase) indicates 12.50 at.% P, 5.19 at.% Rh, and 82.31 at.% Pt.

Note, in the 2nd set of experiments with the Pt-30Rh sample treated in the CO environment, zone 3 is not present (Fig. 12(a)). The EDS area scans of the melted layer (including the needle-like phase) show 12.50 at.% P, 5.19 at.% Rh, and 82.31 at.% Pt. This indicates P-enrichment in the Pt matrix, which causes melting (Fig. 12(b)).

The overall mechanisms of the Pt-Rh alloy degradation by P-bearing gas are schematically summarized in Fig. 13 and Fig. 14. When Pt-Rh alloys with low Rh content (Fig. 13) are exposed to P-rich gas: (1) P first migrates into the alloy through grain boundaries; (2) P reacts with Rh (by consuming Rh) from the grains, forming PRh_2 at grain boundaries; and (3) the remaining P-rich and Rh-poor Pt melts due to further P enrichment, leading to sensor failure.

Fig. 13. Schematic illustrations of the Pt-6Rh (low Rh) alloy failure by P-bearing gas.

When Pt-Rh alloys with high Rh content (Fig. 14) are exposed to P-bearing gas: (1) P diffuses directly into the lattice; (2) PRh_2 forms in the grains as P diffusion proceeds; and finally (3) with further P diffusion, the remaining P-rich and Rh-poor Pt at the P-richer interface with gas liquefies, leading to sensor failure.

Fig. 14. Schematic illustrations of the Pt-30Rh (high Rh) alloy failure by P-bearing gas.

A phosphorus diffusion coefficient in Pt or Rh is not available in the literature. In order to determine the Pt-Rh failure kinetics, the following approach was taken to estimate diffusivity of P in Pt-30Rh. In the most P affected part of the Pt-30Rh wire, the distance from the wire center to the point where the presence of PRh_2 was visually measured, assuming all P diffused into lattice reacted with Rh and formed PRh_2 . Note this assumption is supported by the fact that it is the spatial limit where P is found in grains by SEM-EDX. By subtracting this distance from the original wire radius, the diffusion distance was estimated. In order to provide a rough approximation of the P diffusivity associated with the present work, the nominal diffusion distance of P in the Pt-30Rh lattice was determined using an average of 10 distance measurements. Measurement uncertainty is estimated to be 2 % of the measured distance. The P diffusion coefficient is then estimated from equation (1):

$$l = \sqrt{D \times t} \quad (1)$$

where l is the nominal distance, D is the lattice diffusion coefficient of P, and t is the time. The nominal distance of atoms is defined as the distance where the concentration of traveling atoms becomes half of the surface value, and therefore is considered to be an average distance of atoms that can travel in a given time, t [23]. The time in this calculation is assumed to be equal to the exposure time, which is determined to be 99.5 min for the sample treated in the CO gas environment, and 112.8 min in the CO/CO₂ environment using the thermocouple failure temperature and the beginning temperature of the P-rich gas evolution (~ 700 °C, [18]). Diffusion coefficients of P in Pt-30Rh are estimated to be 3.9×10^{-8} cm²/sec in CO and 3.5×10^{-8} cm²/sec in CO/CO₂. Note the values are a non-isothermal approximation between the gas evolution starting temperature (~ 700 °C) and the failure temperature (~ 950 °C). Those diffusivity values would be smaller if the P gas evolution temperature would be lower due to the presence of carbon in the atmospheres used in this work. The estimated values are found to be larger than the diffusion coefficient of P in fcc-Fe at 950 °C (~ 10^{-10} cm²/sec) [24], whose crystal structure is the same as the Pt alloys. The relatively rapid diffusion of P through Pt under the conditions studied is likely driven by the presence of Rh in the alloy.

4.3. Morphology of the PRh₂ phase

Morphology of the PRh₂ phase varies from lamellar-type for Pt-6Rh to blocky for Pt-30Rh as noted in Fig. 7, Fig. 11 and Fig. 12. This may be attributed to the different diffusion mechanisms. In the Pt-6Rh alloy, P atoms diffuses through grain boundaries and lowers the melting temperature of the grain boundaries while attracting Rh from the grains to form PRh₂ in the Pt-P liquid solution. In the Pt-30Rh alloy, on the other hand, P atoms diffuse through lattice and form PRh₂ in the grains. In this case, Pt atoms are rejected into the matrix while Rh atoms are accepted into PRh₂ during the formation of PRh₂. Interdiffusion through the solid matrix reflects the attainment of local equilibrium at the interface between PRh₂ and the matrix.

5. Conclusion

The failure mechanisms of the Pt-Rh based sensor alloys exposed to a P-rich gas in simulated gasifier environments were investigated. SEM-EDS analysis of the failed thermocouple alloys indicated P reactions with Rh and P migration into the Pt wire where Rh was consumed from the grains, forming the PRh₂ phase. Two distinct failure mechanisms driven by the P-diffusion into the alloys depending on Rh content, were found: 1) the intergranular diffusion mechanism in Pt-6wt.% Rh; and 2) the intragranular diffusion mechanism in Pt-30wt.%Rh. The sensor failure occurred as grains were consumed through interactions with incoming P while grain boundaries liquefy due to the P-enrichment in the Pt matrix. The Pt-Rh-P phase equilibria were discussed based on SEM-EDS analysis. Models of the Pt-Rh based sensor degradation by P-rich gas were proposed.

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Figure and Table captions:

Fig. 1. Experimental set-up used in the present work.

Fig. 2. Type B thermocouple temperature readings caused by exposure to: (a) P-rich CO environment, heated to 1500 °C and cooled to room temperature; (b) P-rich CO/CO₂ environment, heated to 1500 °C and cooled to room temperature; (c) water quenched at sensor failure during heating in the P-rich CO environment; and (d) water quenched at sensor failure during heating in the P-rich CO/CO₂ environment.

Fig. 3. Type B thermocouple temperature readings in the CO/CO₂ gas mixture without aluminum phosphate.

Fig. 4. Cross-sectional optical images of the thermocouple wires heated to 1500 °C and cooled to room temperature in alumina tubes treated: (a) in CO; and (b) in CO/CO₂. Note spheres shown in (b) are not cross-section.

Fig. 5. SEM backscattered electron images of the cross-sectioned thermocouple wires heated to 1500 °C and cooled to room temperature: (a) Pt-6Rh treated in CO; (b) Pt-6Rh treated in CO/CO₂; (c) Pt-30Rh treated in CO; (d) Pt-30Rh treated in CO/CO₂. PRh₂ and P₂Pt chemistry is shown in Table 2. Matrix in (a) and (b) is Rh poor Pt enriched with P, and that in (c) and (d) is Rh deficient Pt.

Fig. 6. Optical images of the longitudinally cross-sectioned thermocouple wires of: (a) Pt-6Rh in CO; (b) Pt-6Rh in CO/CO₂; (c) Pt-30Rh in CO; and (d) Pt-30Rh in CO/CO₂, quenched at failure during heating.

Fig. 7. SEM backscattered electron images of the longitudinally cross-sectioned thermocouple wires of: (a) Pt-6Rh in CO; (b) Pt-6Rh in CO/CO₂; (c) Pt-30Rh in CO; and (d) Pt-30Rh in CO/CO₂, quenched at failure during heating. PRh₂ chemistry is given in Table 2.

Fig. 8. XRD patterns of the cross-sectioned samples treated in the P-rich CO environment: (a) Pt-6Rh wire quenched at 950 °C; (b) Pt-30Rh wire quenched at 950 °C; (c) Pt-6Rh wire slow heated/cooled from 1500 °C; and (d) Pt-30Rh wire slow heated/cooled from 1500 °C.

Fig. 9. Phase compositions for the quenched Pt-Rh wires exposed in P-bearing gases: (a) Pt-6Rh in CO and CO/CO₂; and (b) Pt-30Rh in CO and CO/CO₂. Lines indicate equilibrium tie lines between PRh₂ and the matrix.

Fig. 10. Binary phase diagrams of: (a) P-Rh [20]; and (b) P-Pt [21]. Arrows indicate chemistries of PRh₂ and P₂Pt determined from elemental ratios of Pt, Rh, and P assuming substitutional solutions (Table 2).

Fig. 11. SEM backscatter images of the cross-sectioned thermocouple wires: (a) Pt-6Rh in CO; and (b) Pt-6Rh in CO/CO₂, quenched at failure during heating. EDS area scans of the melted layer (including the needle-like phase) indicates 12.51 at.% P, 11.57 at.% Rh, and 75.82 at.% Pt.

Fig. 12. SEM backscatter images of the cross-sectioned thermocouple wires: (a) Pt-30Rh in CO; and (b) Pt-30Rh in CO/CO₂, quenched at failure during heating. Zone 1: the initial PRh₂ formation in the Pt-Rh lattice. Zone 2: liquid coexisting with PRh₂. Zone 3: the outmost melted layer of Pt saturated with P. EDS area scans of the melted layer (including the needle-like phase) indicates 12.50 at.% P, 5.19 at.% Rh, and 82.31 at.% Pt.

Fig. 13. Schematic illustrations of the Pt-6Rh (low Rh) alloy failure by P-bearing gas.

Fig. 14. Schematic illustrations of the Pt-30Rh (high Rh) alloy failure by P-bearing gas.

Table 1. Experimental conditions used in this work.

Table 2. Averaged SEM-EDS elemental analysis of the solid phases formed in the Pt-Rh_x wires (at.%).