On the Reaction between Platinum and Sulfur, Selenium, or Tellurium. I. Preparation of PtS, PtSe$_{0.80}$, and PtTe

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The direct syntheses of PtS, PtSe$_{0.80}$ and PtTe from different materials of platinum have been studied by means of X-ray and metallographic methods in the temperature region 700—1 150°C. While these compounds are easily prepared from powdered platinum in this temperature range, the results are dependent upon temperature for platinum plate or wire. At temperatures below the melting point of the compounds layers of di- and "mono"-chalkogenides are formed on the platinum plates and platinum wires during the reaction. The reaction apparently ceases when one half of the platinum has reacted. A possible explanation is proposed in terms of the existing theories for oxidation.

The reaction of sulfur, selenium and tellurium with platinum to form platinum "mono"-chalkogenides has been studied by many investigators [1-11]. A literature survey of the earlier studies on the platinum chalkogenides has been given by Grønvold et al.[1] According to Grønvold et al.[1], compounds with formal oxidation number +2 (+8/5) and +4 were found to exist by means of X-ray and density measurements, cf. Table 1. While "mono"-chalkogenides can be easily obtained from fine powdered platinum [1], attempts to make "mono"-chalkogenides from platinum plate or wire resulted in heterogeneous products with platinum and platinum di-chalkogenides as main constituents.

The published data indicate that the nature of the platinum metal is of fundamental importance in the reaction and new experiments were carried out to examine the difference between powdered platinum, platinum plate and platinum wire.

EXPERIMENTAL

Most of the platinum metal used in this study was platinum wire from Johnsen Matthey & Co., Ltd. A spectrographic analysis of the platinum showed about 0.05 % Au, 0.05 % Cu, 0.02 % Ir, 0.01 % Pd and 0.01 % Rh. No analysis was made on gaseous impurities (O$_2$, N$_2$, H$_2$) and carbon.

Sulfur from Schering-Kahlbaum A. G. (Sulfur cryst. puriss.) was purified by double distillation in a silica apparatus. Only the middle fractions were used. The highly purified

Table 1. Crystallographic data for the platinum chalkogenides.

Phase	Structure type	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\beta(°)$
PtS	B 17	3.4700		6.1096	
PtS$_2$	C 6	3.5432		5.0388	
Pt$_{10}$Se$_8$	MONOCL.	6.5806	4.6248	11.145	78.40
PtSe$_2$	C 6	3.7278		5.0813	
PtTe	ORTHOR.	6.6144	5.6360	11.865	
PtTe$_2$	C 6	4.0259		5.2209	

selenium was a gift from Bolidens Gruvaktiebolag, Sweden. It carried the analysis: 0.0002 % Cu, 0.0007 % Fe, 0.003 % Te, 0.01 % S and 0.003 % non volatile matter. Tellurium from The British Drug Houses Ltd. was purified by vacuum distillation in a silica apparatus. According to the spectrographic analysis the distilled product contained less than 0.01 % Fe and only traces of Al, Mg and Pb.

The samples were prepared by heating accurately weighed quantities of platinum and sulfur, selenium or tellurium, respectively, in evacuated and sealed, transparent silica tubes. Before each experiment the platinum specimens were degreased in chloroform and acetone, and finally rinsed in distilled water. The platinum wire, with diameter 0.45 mm, was cut into specimens about 30 mm long. The platinum sheets were cut into specimens about 10 × 3 × 0.2 mm.

The reaction of platinum with sulfur, selenium or tellurium was studied at temperatures between 700 and 1 150°C. By means of a variac the temperature of the heating furnace was kept constant within ± 5°C. The Pt/Pt-Rh thermocouple of the furnace was calibrated with a standard couple. Before the start of the run, the furnace was at room temperature. The furnace reached the desired temperature in a period of about one hour.

The X-ray diffraction investigation of the reaction products was carried out in powder cameras with 114.6 mm effective diameter, using filtered CuK-radiation. X-Ray photographs were taken on samples both from the total amount of the platinum chalkogenide scales and from different layers of the heterogeneous reaction product.

The thickness of the unreacted nucleus of platinum was measured with a micrometer.

The preparation of metallographic specimens proved difficult as the brittle chalkogenide layer became crushed and displaced during the grinding and polishing. The procedure which was adopted was to use araldite as the mounting material. After grinding, polishing with a fine grained diamond paste and final polishing with levigated alumina, transverse sections of the specimens were examined.

The microindentation hardness testing was performed with a Reichert microhardness tester (No. 1109) used in connection with a Reichert universal camera microscope (model MeF). The indenter was a Vickers pyramid. Variations in microhardness at a single load over transverse sections of the specimens were recorded. A comparatively low load — 8.4 g — was chosen. The cross sections to be tested, were always etched in 10 % NaCN + 10 % (NH$_4$)$_2$S$_2$O$_8$ (1 : 1 by volume) prior to the hardness measurements.

RESULTS

A. Fine powdered platinum

In agreement with the results of Grønvold et al.[1] both the "mono"-chalkogenides and the di-chalkogenides of platinum could be easily prepared from fine powdered platinum. According to the present results the reactions were

completed and homogeneous samples were obtained after heat treatment at 825°C for 2—4 days, depending on the chalkogen used.

The "mono"-chalkogenides PtS, $PtSe_{0.80}$ and PtTe were also obtained by adding platinum in the right proportion to the di-compounds and heating the samples at 825°C for 5 days.

B. Platinum sheet or wire

Melted samples. X-Ray powder photographs of melted alloys with composition $PtSe_{0.80}$, prepared from platinum sheet or wire and selenium showed the presence of Pt, $PtSe_{0.80}$ and $PtSe_2$. In agreement with the results of Grønvold *et al.*[1] this sample became homogenized on heating the finely ground alloys at 825°C, which is below the peritectic temperature.

According to the present results PtTe was obtained from platinum plate or wire and tellurium heated to the melting point or just below.

Attempts to synthesize the PtS phase by a similar method from the same platinum material failed, because PtS decomposes instead of melting. Neither could the samples be heated to a sufficiently high temperature since the sulfur pressure [4,12,13] made the quartz tubes burst.

Below the melting points. Experiments were made in the temperature region below 1 100°C for PtS and $PtSe_{0.80}$ and below 900°C for PtTe. The characteristic feature of these experiments is the growth after a short time of coatings of platinum chalkogenides on the plates and wires. The platinum chalkogenides form well adherent coatings. Unlike many other metal chalkogenide coatings these coatings did not spall during or after cooling of the specimens down to room temperature.

The results of the thickness measurements for the unreacted nucleus of the platinum wires are listed in Table 2. The thickness of the nucleus is found

Table 2. Thicknesses of unreacted platinum in platinum wires.

Sample	Melting point (°C)	Temperature (°C)	Thickness (mm) of platinum nucleus after			X-Ray photographs of layers show
			10 days	30 days	50 days	
PtS	Decomposes	700	0.43	0.43	0.43	PtS
		825	0.32	0.32	0.32	$90-95$ % PtS_2
		1 000		0.32		$10-\ 5$ % PtS
$PtSe_{0.80}$	$1\ 055 \pm 15$	825	0.35	0.34	0.34	$85-90$ % $PtSe_2$
		1 000		0.34	0.34	$15-10$ % $PtSe_{0.80}$
PtTe	925 ± 15	700		0.32	0.31	$90-95$ % $PtTe_2$
		825	0.31	0.31	0.31	$10-\ 5$ % PtTe
		900	Homogeneous product			PtTe

to be ≈ 0.32 mm, *i.e.*, nearly equal to the value $\dfrac{1}{\sqrt{2}}\, d\left(\dfrac{1}{\sqrt{2}}\, 0.45 \approx 0.32\right)$ one would expect to find when one half of the platinum has reacted. The thickness of the unreacted nucleus does not change within the limits of the experimental error after ten days, *cf.* Table 2. Since no visible amounts of the metalloids are seen in the tubes a reaction of the type:

$$Pt + X_2 = PtX_2 \quad (X = S, Se \text{ or } Te)$$

is expected to have taken place.

X-Ray photographs of the platinum chalkogenide layers show that two phases are present. According to the X-ray photographs 90—95 % is found to be di-chalkogenides (PtS_2, $PtSe_2$ or $PtTe_2$) and 10—5 % "mono"-chalkogenides (PtS, $PtSe_{0.80}$ or PtTe). The X-ray results are accordingly in close agreement with the results of the thickness measurements.

Further X-ray studies indicate that the chalkogenide coatings are composed of two different layers. Fig. 1a is a drawing of the idealized distribution of the layers found on a sulfurized platinum wire. Next to the platinum core is found the PtS layer and further away the PtS_2 layer. A similar distribution of layers is found in the experiments to prepare $PtSe_{0.80}$ and PtTe. When platinum and tellurium react at 900 °C the X-ray photographs taken of the reaction product show that only PtTe is present. Fig. 1b shows the results which indicate that the wire form is preserved, while a hole appears in the centre of the wire. Similar holes seem also to be present in samples of PtS_2, $PtSe_2$ and $PtTe_2$, prepared from platinum sheet. The same was evidently also observed by Thomassen [9] by the preparation of platinum di-chalkogenides from platinum plates.

The surface appearance of the reacted specimens is dependent upon the reagent (sulfur, selenium or tellurium), temperature, pressure and the duration of the reaction. Initially the platinum chalkogenides formed do not lead to continuous chalkogenide scales, but nucleation of the platinum chalkogenides takes place in spots on the surface.

After a short time layers of a rather uniform thickness have grown up on the plates and wires. Fig. 2a shows a platinum sheet heated with sulfur for 1 day at 825°C. X-Ray photographs of the platinum sulfide layer gave the picture of the PtS_2-phase and the strongest reflections from the PtS-phase. At 700°C (*cf.* Table 2) this sulfide layer does not increase much in thickness
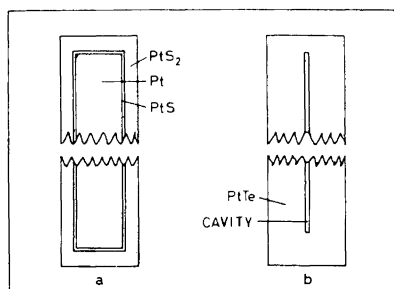

Fig. 1. The idealized distribution of the platinum chalkogenide layers on a platinum wire viewed in centralincision. *a,* Weighed quantities correspond to PtS. Temperature 825°C; *b,* PtTe prepared at 900°C.
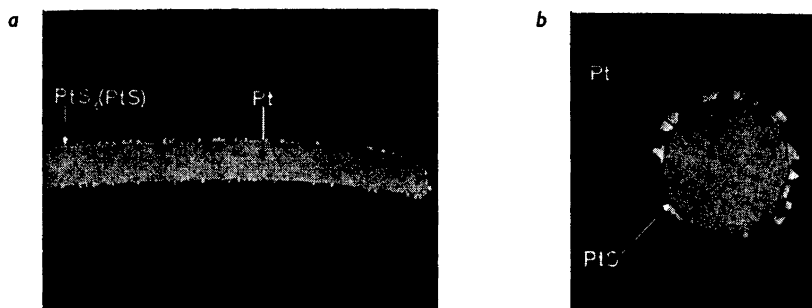
Fig. 2. Metallographic cross-section of platinum specimen heated with sulfur for *a*, 1 day at 825°C; *b*, 50 days at 700°C. Polarized light. 40 ×.

with time. Fig. 2b shows the cross-section of a platinum wire heated with sulfur for 50 days at 700°C.

Prolonged heating at higher temperatures leads to thick, well adherent platinum chalkogenide scales. The appearance of platinum sheet specimens after heat treatment at 825°C with selenium and tellurium is shown in Figs. 3a and b, respectively. In the case of platinum wire a distinct splitting of the di-chalkogenide layer along the wire is seen. Figs. 4a and b show cross section of wires heated with selenium and tellurium, respectively. As might be seen from the pictures, a preferred orientation normal to the metal surface is generally found in the "mono"-chalkogenide layers while recrystallization has taken place in the di-chalkogenide layers.

All the micrographs discussed so far, *cf.* Figs. 2—4, are from samples with weighed quantities corresponding to the "mono"-chalkogenides. Figs. 5a and b show the cross section of a platinum wire heated with a selenium amount corresponding to the formula $PtSe_{1.75}$ for 10 days at 825°C. The occurrence of the characteristic splitting is still more pronounced throughout the $PtSe_2$ layer in this sample.
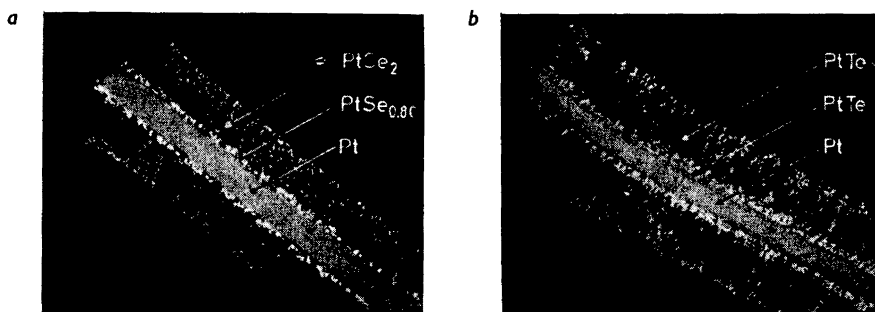

Fig. 3. Metallographic cross-section of platinum specimen heated with *a*, selenium (weighed quantities corresponds to $PtSe_{0.80}$); *b*, tellurium (weighed quantities corresponds to PtTe) for 10 days at 825°C. Polarized light. Platinum sheet turned 45° to incident beam. 40 ×.

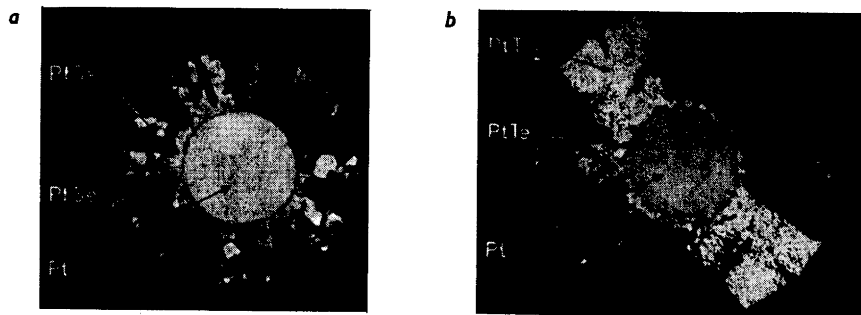*Fig. 4.* Cross-section of platinum wire heated with *a,* selenium (weighed quantities corresponds to $PtSe_{0.80}$); *b,* tellurium (weighed quantities corresponds to PtTe) for 10 days at 825°C. Polarized light. 40 ×.

The results of the micro indentation hardness measurements in the metal core show an increase in the hardness near the platinum/platinum chalkogenide interface. Except for the platinum telluride samples the depth of contamination is found to be about 5—10 μ. The hardness curve for a representative platinum/platinum telluride sample is found in Fig. 6.

DISCUSSION

From thermodynamic reasoning one might expect to find in the case of the reaction between platinum and sulfur, selenium, or tellurium, a sequence of the platinum chalkogenides in the layers with the "mono"-chalkogenides near the platinum/platinum chalkogenide phase boundary and the di-chalkogenides in the outer part of the layers. Both the X-ray diffraction and metallographic studies show that this occurs.

A mixture of platinum metal and one of the platinum di-chalkogenides is thermodynamically unstable at the temperatures in question. The reason
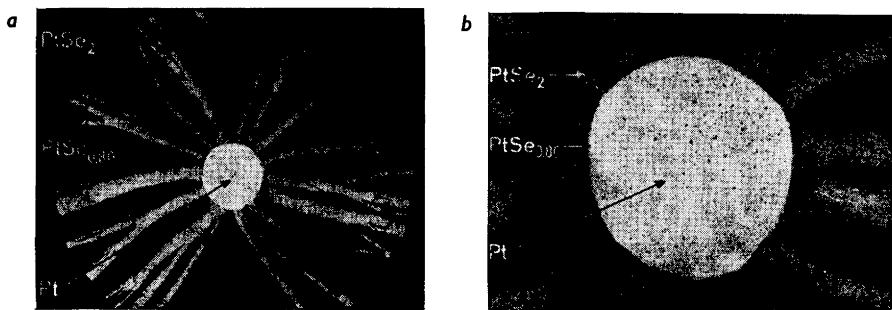

Fig. 5. Cross-section of platinum wire heated with selenium for 10 days at 825°C. Vertical illumination. *a,* 40 ×; *b,* 125 ×.
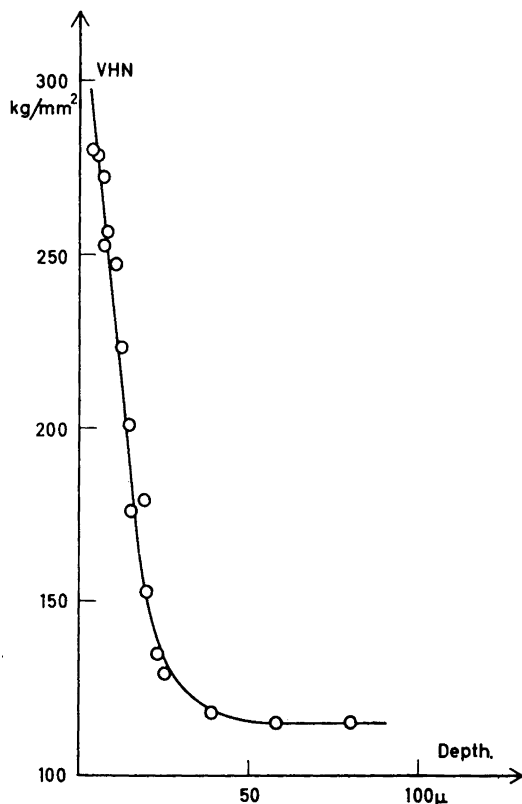
Fig. 6. Micro indentation hardness *versus* depth for a platinum sheet heated with tellurium for 10 days at 825°C.

why a reaction to form the "mono"-chalkogenides does not take place rapidly is that the reactants are separated by the intermediate layer of the "mono"-chalkogenides. Actually the reaction has to occur by diffusion of ions and electrons through the "mono"-chalkogenide layers and by reactions in the phase boundaries, *cf.* Fig. 7. Because of the observed holes in the samples of PtS_2, $PtSe_2$, $PtTe_2$ and $PtTe$ (900°C) there are reasons for assuming
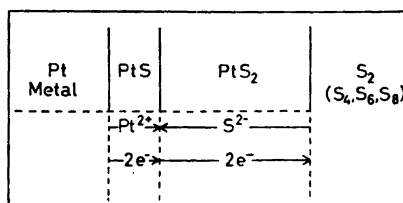

Fig. 7. A possible model for diffusion of ions and electrons in the platinum sulfide layers.

that platinum atoms or ions and electrons migrate through the "mono"-chalkogenide layers. Sulfur, selenium or tellurium atoms or ions and electrons diffuse in the di-chalkogenide layers. When unreacted sulfur, selenium or tellurium is present there is a considerable vapour pressure in the tubes. This pressure drops to the equilibrium pressure platinum di-chalkogenide/platinum "mono"-chalkogenide when the reaction to di-chalkogenide (and small amount of "mono"-chalkogenide) is completed. On the basis of the existing theories of oxidation the reaction velocity should be dependent upon this pressure. A considerably smaller rate might thus be expected from the moment no more unreacted sulfur, selenium or tellurium is left.

From the present study further information about the diffusion of atoms in the chalkogenide layers and reactions in the phase boundaries can not be obtained. It is, however, planned to carry out a detailed study of the kinetics of these reactions and to determine the ratelimiting step.

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