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Atomic-layer by atomic-layer compositional depth profiling: Surface segregation and impurity cosegregation of Pt-Rh and Pt-Ru alloys

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Absolute composition depth profiles of true single-atomic-layer depth resolution have been obtained for the near surface layers of the (001) and (111) planes of Pt-Rh and Pt-Ru alloys in surface segregation and cosegregation with sulfur of these alloys. For both alloys, the segregation species is found to be Pt, and its concentration approaches the bulk value nonmonotonically; the composition of the second layer is reversed. We did not detect a significant dependence of surface segregation on crystal planes and also find the plane-edge effect to be very small for Pt-Rh alloy. Also no reversed segregation at the two dilute ends of the alloy composition of Pt-Rh is found. For Pt-Rh, if the sample contains a very small amount of sulfur, then sulfur and Rh cosegregate to the surface, with sulfur forming an adsorption overlayer. This reversal of segregation species by impurity sulfur is not observed for Pt-Ru alloys. We believe that atom-probe composition depth profiles can also be used as references for calibrating other surface analytical techniques.

I. INTRODUCTION

Atomic-layer by atomic-layer compositional analysis of surfaces has always been one of the major endeavors in surface science. Usually the composition of a surface can be analyzed with surface-electron or ion spectroscopy combined with ion sputtering etching of the surface layers. Despite continuous efforts for over 20 years, however, there is not a single macroscopic technique which has succeeded in either achieving true atomic-layer depth resolution in compositional depth profiling, or in determining the absolute composition of surface layers. The low-energy ion scattering method can provide composition of the top surface layer, and only in limited cases also the second layer.[1] There is a microscopic technique, time-of-flight atom-probe field ion microscopy, which has long succeeded in obtaining absolute composition depth profiles of alloy surfaces with true atomic-layer depth resolution in a study of surface segregation and impurity cosegregation.[2,3] When we started the (time-of-flight) TOF atom-probe analysis of surface layers about ten years ago, we also intended to make available reference data useful for calibrating macroscopic surface analytical techniques. Although our data can indeed be used for such purposes and there is also such a need, so far this intention of ours has not been realized. Our studies have nevertheless provided valuable data for understanding surface segregation and impurity cosegregation phenomena.[4,5]

Surface segregation and impurity segregation are well-known interface segregation phenomena which have many basic and practical interests.[6,7] They are particularly important for a basic understanding of interfacial segregation phenomena[8,9] as the solid-vacuum interface should be one of the simplest interfaces for theoretical treatments. Interface segregation is known to affect the strength and metallurgical properties of materials in a very profound way.[8] As already mentioned, although there are many surface analytical techniques capable of analyzing the composition of surface layers, there is really only one which can give truly atomic-layer by atomic-layer compositional analysis of surfaces. Here we report a TOF atom-probe study of surface segregation and impurity cosegregation with sulfur of the (111) and (001) surfaces of Pt-Rh and Pt-Ru alloys.

There are at least two reasons for these alloy systems to be of particular interest. From the technical point of view, Pt, Rh, and Ru all have a similar evaporation field.[10] Thus in atom-probe analysis, there will be no artifact by preferential field evaporation of one of the species in the alloys by the dc holding field. Preferential dc field evaporation of a species will of course produce an incorrect composition of the surface. This is a very important point if atom-probe data are eventually to be accepted as references for calibrating other macroscopic surface analytical techniques. From a scientific point of view, both constituents in these two alloy systems are noble metals. Dynamics of interface segregation of such alloys should be theoretically interesting and can be probed by composition depth profiling of near-surface layers. Also, both these alloys are important catalysts in the chemical industry.[11–13] Surface segregation and impurity cosegregation will change the chemisorption behavior as well as the catalytic activity and selectivity of these alloys. Pt-Rh alloys are used not only as practical catalysts in many industrial processes, but also are widely used in equipment for glass manufacturing and in thermocouples and as heating elements because of their resistance to corrosion and deformation at high temperatures.

There have been several studies of surface segregation of Pt-Rh alloys, using mostly Auger electron spectroscopy (AES).[14–17] An earlier TOF atom-probe study of this system from our laboratory used samples with a small amount of sulfur.[5] Thus the data really reflect cosegregation with sulfur of these alloys. In a recent letter, we have presented some data concerning surface segregation of Pt-Rh alloys with no sulfur impurity.[18] Here we present details of this experiment. In addition, we have also studied surface segregation and sulfur cosegregation of Pt-Ru alloys. As far as we are aware, there are no careful studies of surface segregation and impurity cosegregation of this alloy system. Interface impurity segregation itself is of considerable interest[8] as it will change profoundly the chemical and physical properties of the alloy surface. In addition, it may also change the surface segregation behavior of the alloy.

II. EXPERIMENTAL METHODS AND PROCEDURES

The Pt-Rh alloy samples used in this study are the same as those used by Ahmad *et al.* in an earlier study of ours. They are 4-mil wires containing about 50 ppm or less of sulfur impurity. These wires are first annealed in vacuum in the 10^{-9}-Torr range for ~ 10 h at $\sim 1000\,°\mathrm{C}$ by resistive heating. Field ion tips are then prepared by electrochemical etching in a molten salt of $NaNO_3 + NaCl$, and then carefully washed with distilled water. It is found that a significant segregation of sulfur to the surface can occur for such tips even though they contain only a very small concentration of sulfur, about 50 ppm or less. These sulfur atoms form an adsorption overlayer at the surface. Pretreating these wires by heating them to $\sim 1000\,°\mathrm{C}$ in 1 atm of high-purity oxygen for two to several hours removes sulfur impurities from these samples. No sulfur segregation is found for samples prepared from the pretreated wires.

After a freshly etched tip is installed in the atom probe, it is baked until vacuum in the 10^{-10}-Torr range is reached. The tip is degassed in this vacuum to $\sim 800\,°\mathrm{C}$ for several minutes, and then is dc field evaporated to produce an end form. This surface is then examined in He field ion images to make sure that there are no lattice defects in the sample and a proper identification of crystal planes is then made. The system is baked again until a vacuum of $\sim 2\times 10^{-10}$ Torr is reached. The tip is degassed again and then field evaporated. The tip is then ready to be used for surface segregation studies. Before we discuss how surface layers are analyzed one by one, it is important to make sure that the atom probe gives the correct composition of the sample under the operation conditions under which data are taken. Our atom-probe data are always taken at a very low field evaporation rate, about one ion detected for every 20 high-voltage pulses. The pulse voltage is taken to be about 20% of the total applied voltage. Under such conditions there is no preferential field evaporation of a species by the dc holding voltage.[5] This can be easily checked by analyzing the composition of the bulk. We have carried out this check as shown in Fig. 1. The compositions of all the samples studied, as measured with the atom probe, agree with the nominal compositions of these samples. Since the evaporation fields of Rh and Pt are almost identical,[10] no edge effect is expected. Figure 1 substantiates this conclusion.

For the segregation study the tip is annealed at 700 °C for 5 min in vacuum to equilibrate the distribution of chemical species in the sample and then quenched. The quenching rate is about 10^4 K/s because of the very small volume of the tip and the heat sink of the refrigerator. As we have already discussed repeatedly in our earlier publications, this effectively freezes the spatial distribution of the chemical species equilibrated under the annealing.[5] In an earlier experiment we have already showed with an example that heating at 700 and 800 °C for a Pt-Rh alloy gave practically the same composition depth profile.[5] The diffusivity of atoms in the alloys studied is estimated to be $\sim 0.1-0.3\,\text{Å}^2/\mathrm{s}$ at 700–800 °C. During the quenching, the diffusion length, or the root-mean-square displacement, is less than 0.05–0.2 Å; thus no rearrangement of atoms among surface layers is expected. Within an annealing period, however, the diffusion length is about 10–50 Å.[5] With the very small size of the tip, equilibrium distributions can be reached in the near-surface layers. We have tested with 30 min annealing period without observing a significant change in the depth profiles.[5]

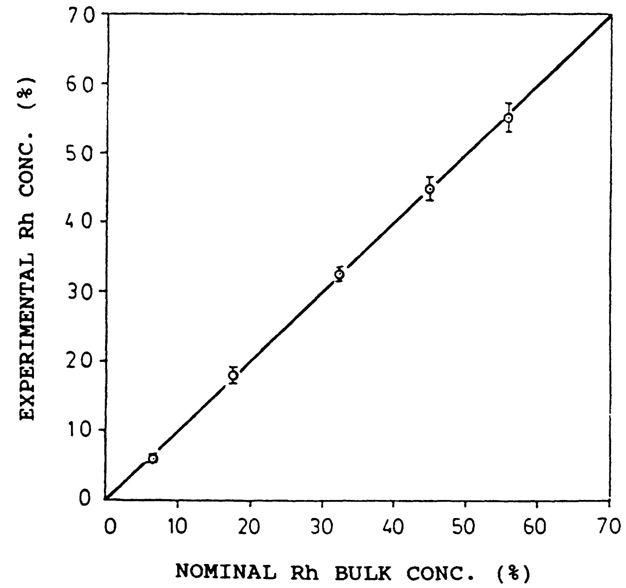


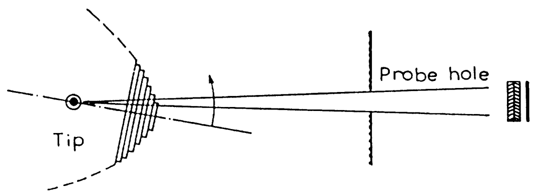
FIG. 1. Atom-probe compositional analysis of five Pt-Rh alloys showing no preferential dc field evaporation of one of the species, and the compositions derived are in good agreement with the nominal compositions.

Atom-probe data are then taken by aiming the probe hole at the very edge of the top layer. As edge of the plane recedes by gradual pulsed field evaporation, the orientation of the tip is gradually adjusted to properly aim the probe hole always at the edge of the top surface layer. When the top layer is gone, ions are then collected from the edge of the second surface layer which has now become the top layer of the surface. By properly sorting these data according to the atomic layers where they are collected, a composition depth profile with true single-atomic-layer depth resolution is achieved. This elaborate procedure and the volume of the alloy tip sampled are illustrated in Fig. 2.

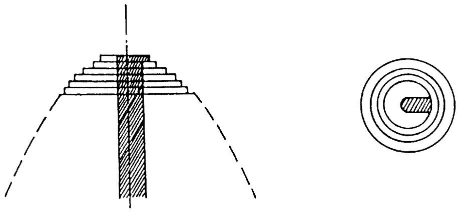
The number of ions collected from one layer is usually quite small, typically less than 50–100 ions for the top layer, and much less for the subsequent layer. In Fig. 3 examples of the atom-probe data are shown for the first five layers for surface segregation of a Pt–17.7 at. % Ru (001) surface and for the first layer for impurity cosegregation of a Pt–5.9 at. % Rh (001) surface. These are what we call lateral concentration profiles. The number of Ru ions detected is plotted against the number of Pt ions detected according to the sequence of their detection. The lateral concentration profile contains information on a possible concentration variation of the alloy species within a surface layer, such as a plane edge effect. To make a set of depth profiles statistically reliable, from several to over ten sets of data are taken under identical experimental conditions. These data are then combined according to the depth of the surface layers. The statistical uncertainty of the composition of each atomic layer is calculated according to

$$\delta = 100\% \, (N_A N_B)^{1/2} / (N_A + N_B)^{3/2} ,$$

where N_A and N_B represent, respectively, the number of A and B atoms detected from that layer. Unless the statistical uncertainty is significantly smaller than the concentration itself, the data cannot be statistically reliable. We always collect from a few hundred to over one thousand ions from one atomic layer. Unfortunately, such attention has not always been achieved in other atom-probe studies of surface segregations.



(a) Sampling Procedure



(b) Volume Sampled, Two Views

FIG. 2. (a) A schematic diagram showing how surface layers are analyzed one at a time. The probe hole is aimed at the edge of the top surface layer when pulsed field evaporation is done. Therefore the detector can only detect atoms from the edge of the top layer. As the top layer reduces in size by gradual pulsed field evaporation, the tip orientation is adjusted accordingly. After the top layer is completely gone, probe hole is then aimed at the edge of the second layer which becomes now the top layer. (b) The cross-sectional view and the top view of the volume of the tip sampled. Only the plane edge of the first layer can be analyzed. From the second layer down, plane-edge atoms are field evaporated before the layer is being analyzed.

The nature of field evaporation and the visual aid of the aiming process contribute to the true atomic-layer depth resolution of the depth profiles we have obtained, which are unique to atom-probe field ion microscopy. In macroscopic surface analytical techniques, a depth resolution is usually defined by the depth where the signal intensity will decay to e^{-1} times that at the surface. In contrast, in the atom probe the depth is defined in terms of atomic layers, not an average value. Thus the depth resolution is absolute. Also atom-probe data involve direct counting of ions and does not involve conversion of signal strengths to abundances of chemical species. Therefore the compositions derived are absolute; a term often used in isotope abundance analyses of elements. We therefore call the composition depth profiles obtained with the TOF atom probe the "absolute composition depth profiles." It is with such elaborate procedures and care that we believe our absolute composition depth profiles in alloy segregation studies can be used as references for calibrating other macroscopic surface analytical techniques.

III. RESULTS AND DISCUSSIONS

A. Surface segregation of Pt-Rh and Pt-Ru alloys

Four questions in surface segregation of Pt-Rh alloys are investigated in this study. The first question is which is the segregation species in a high-purity Pt-Rh and how does the segregant concentration vary in the near surface layers. The second question is whether the segregation species changes at the two dilute ends of the composition of this alloy system. The third is whether there is a strong plane structure dependence of the top layer composition, or equivalently a strong plane edge effect. Finally, whether the segregation species is affected by the

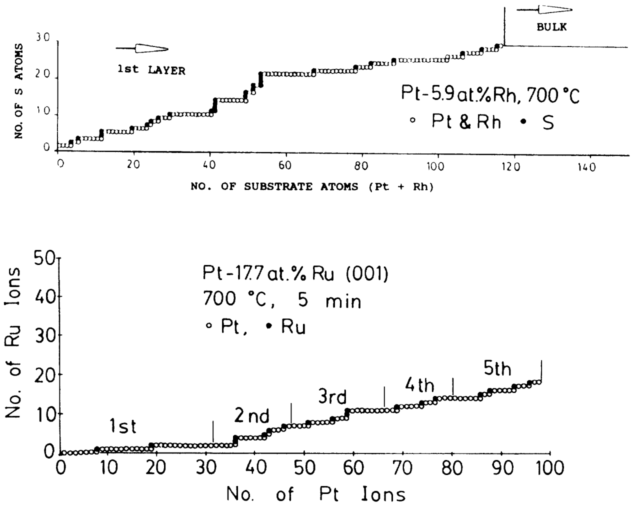


FIG. 3. Lateral composition profiles of a pure Pt–17.7 at. % Ru alloy, and a Pt–5.9 at. % Rh alloy containing less than 50 ppm of sulfur atoms. These alloys have been annealed to 700 °C for 5 min. The bottom diagram shows analysis of five atomic layers, whereas the top diagram shows analysis of only the first layer.

presence of a small amount of impurities such as sulfur, and impurity cosegregation.

In Fig. 4, we show absolute composition depth profiles for the (111) and (001) planes of Pt–44.8 at.% Rh thermally equilibrated at 700 °C for 5 min. That heating at this temperature for 5 min is sufficient to establish thermal equilibration of composition depth profiles of this alloy will become obvious in a later section discussing cosegregation with impurity sulfur. It can be clearly seen from this figure that the top layer is enriched with Pt, whereas the second layer is depleted with Pt. From the third layer on, the composition returns to the bulk value. Thus the segregant concentration decays into the bulk nonmonotonically, very possibly oscillatory,[3] which has also been considered theoretically.[19]

It is generally found and accepted that the degree of surface segregation depends on the atomic structure of the surface; the degree of segregation is expected to be larger for less closely packed surfaces.[20,21] According to Fig. 4, for Pt–44.8 at.% Rh, the Pt concentration at the top layer of the (111) plane is 73.2±5.0 at.%, whereas for the (001) surface it is 71.1±6.0 at.%. Thus within the statistical uncertainties of these data, this alloy does not show a significant difference in the degree of surface segregation of the two surfaces. This is consistent with a plane edge effect we have investigated as will be discussed later. In contrast, for Ni-Cu alloys, the less closely packed planes show significantly larger segregant, Cu, concentration.[20,21]

It has recently been claimed that a reversed segregation can occur for dilute alloys at the two ends of the alloy composition. Thus in $Ni_{1-x}Cu$, Cu segregates to the surface if $x < 0.84$. If $x > 0.84$, the segregation species is reversed to Ni.[22] Note only are the statistics of the data very unreliable, but also such a feature could have been produced by an artifact of a preferential dc field evaporation of Cu atoms as has been discussed earlier. Therefore we decided to look into such a feature in Pt-Rh where we have carefully established that there will be no preferential dc field evaporation of a species under the operation condition of the atom probe. Since in Pt-Rh alloys the segregation species is Pt, one would expect a reversal to Rh for dilute alloys. Figure 5 shows a composition depth profile of Pt–6.4 at.% Rh. As can be seen from this figure, the segregation species remains Pt. We must conclude that we do not find a reversed segregation at the dilute Rh end of the composition of this alloy system. This result clearly shows that the observation of a reversed segregation in Ni-Cu alloys is either a specific behavior of that alloy system, or more likely an artifact of that experiment. It is not a surface segregation behavior of alloy systems in general.

An important question is whether surface segregation is enhanced at the edge of a plane. In fact, many investigators suspect the validity of comparing surface composition depth profiles obtained from field ion tips with those derived in macroscopic experiments. They argue that the size of the surfaces on a field ion emitter is so much smaller that comparing them with macroscopic surfaces is inappropriate.[21] Such an argument is equivalent to saying that there should be a very strong plane edge effect in surface segregation. The advantage of the TOF atom probe in surface segregation study is of course the possibility of studying plane edge effects if they exist. In TOF experiments, plane edge effects will in principle show up readily in the lateral concentration profile. However, due to the very small effect, we have never observed a clear feature of a plane edge effect in the lateral concentration profiles of all the alloys we have investigated so far, except when a Ni-Cu alloy is annealed in the presence of nitrogen gas in which the Cu concentration is greatly enhanced near the plane edge.[23] We decided to examine the first few ions detected from the plane edge of the top surface layer right after each annealing of the alloys. For the (111) plane, from 20 sets of data collected, Pt concentration is found to be 78.3±5.3 at.% from the first three

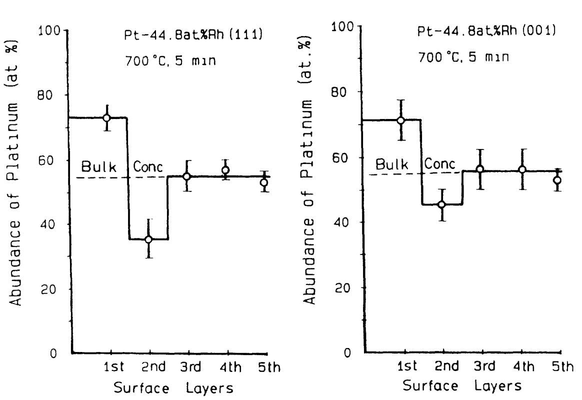


FIG. 4. Composition depth profiles of the (111) and (001) planes of Pt–44.8 at.% Rh alloy. Note that the top surface layers are enriched with Pt, the second layers are depleted with Pt, and from the third layer on, the composition returns to the bulk value.

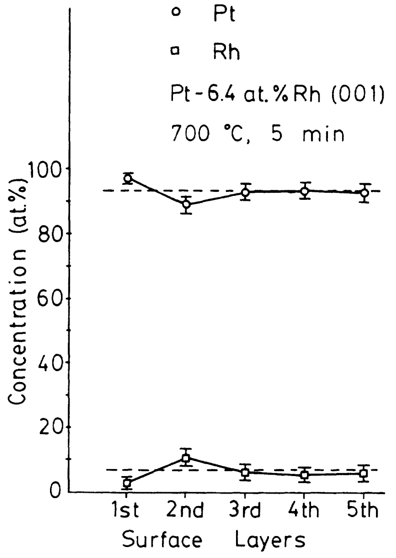


FIG. 5. A composition depth profile of the (001) plane of Pt–6.4 at.% Rh alloy. Note the segregation species remains Pt, and there is no reversal of segregation behavior of this dilute alloy of Rh.

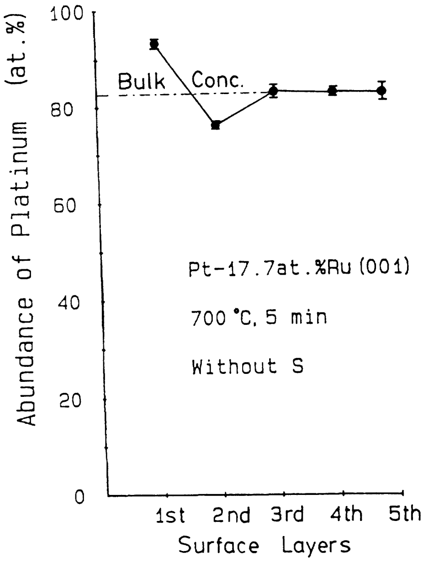


FIG. 6. A composition depth profile of the (001) plane of Pt–17.7 at. % Ru. The segregation behavior of this alloy is almost identical to that of Pt-Rh alloys.

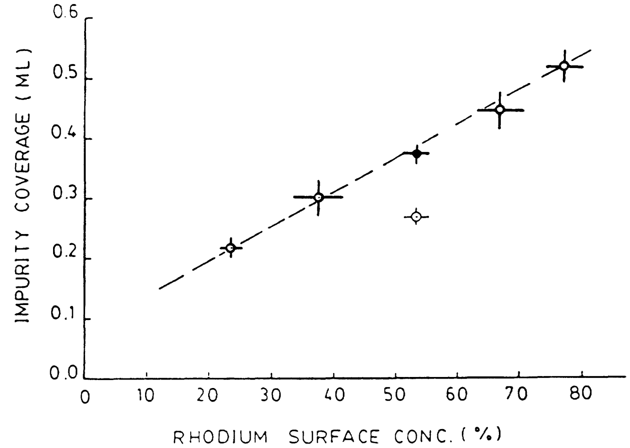


FIG. 8. The concentration of Rh in the top layer is found to be linearly proportional to the coverage of sulfur in the overlayer, signifying a direct correlation of Rh segregation to the impurity segregation. One of the samples contains a small amount of impurity As. For this sample, the total impurity concentration is represented by the solid circle.

ions detected in each set. This is only slightly higher than the 73.2±5.0 at. % of the average concentration of the first layer if one considers the rather large statistical uncertainty of this data. For the (001) plane, from 23 sets of data collected, the Pt concentration is found to be 82.6±4.6 at. % which is also slightly higher than the 71.1±6.0 at. % of the average concentration of the first layer. Thus a plane edge effect is clearly seen even though it is quite small. As three ions constitute only about 5–10 % of the total ions collected from a top surface layer and the rather small plane edge effect detected, the overall inaccuracy in the determination of the composition of the top surface layer by ignoring the plane edge effect is negligibly small. We therefore conclude that TOF atom-probe data are a reliable and approximate well those of macroscopic surfaces. These data can indeed be used as references in calibrating macroscopic surface analytical techniques.

In connection with cosegregation of Pt-based alloys

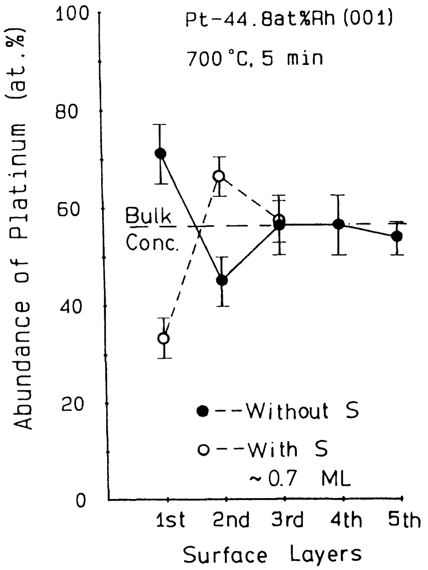


FIG. 7. A comparison of the surface segregation behaviors of two Pt-Rh alloys of the same bulk composition, but one with about 50 ppm of impurity sulfur. Note the surface segregation behavior is completely reversed by cosegregation with sulfur. Sulfur atoms segregate to the surface to form an overlayer.

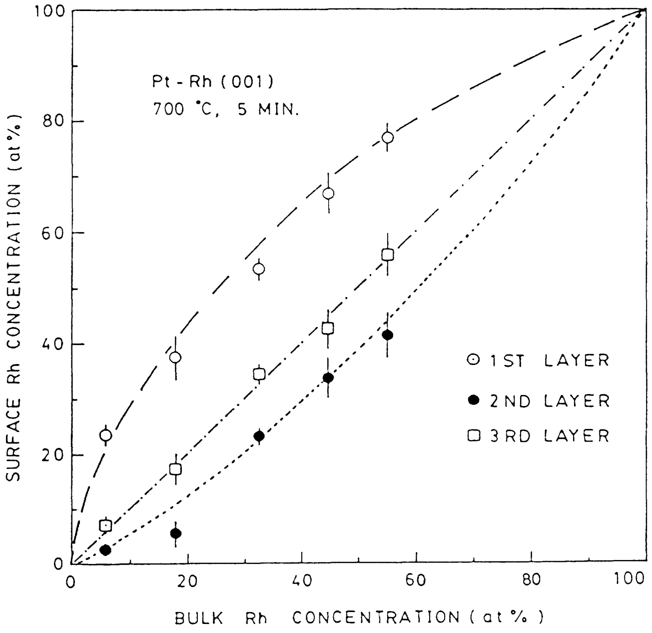


FIG. 9. All five Pt-Rh alloys containing a trace of sulfur show similar surface segregation behavior which is completely reversed from alloys containing no impurity atoms.

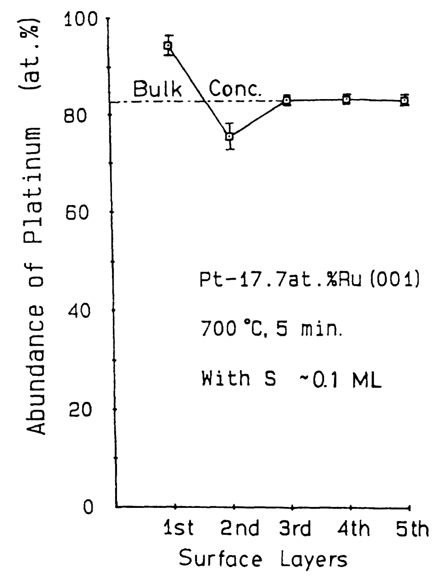


FIG. 10. Sulfur atoms do not seem to change significantly the surface segregation behavior of Pt-Ru alloy. Thus this composition depth profile is almost identical to that shown in Fig. 6.

with sulfur impurities, we have also investigated surface segregation of Pt–17.7 at. % Ru alloy. Pt-Ru alloys are also one of the important catalysts. From a technical point of view, Pt and Ru have a similar evaporation field, therefore no preferential dc field evaporation of a species will occur. Figure 6 shows an absolute composition depth profile for the (001) plane of the alloy annealed at 700 °C. The segregation species is found to be Pt and again the concentration of Pt decays nonmonotonically into the bulk value in about two atomic layers. Thus in every aspect surface segregation of this alloy is very similar to Pt-Rh. This is not so when cosegregation with sulfur is involved, as will become clear in the next section.

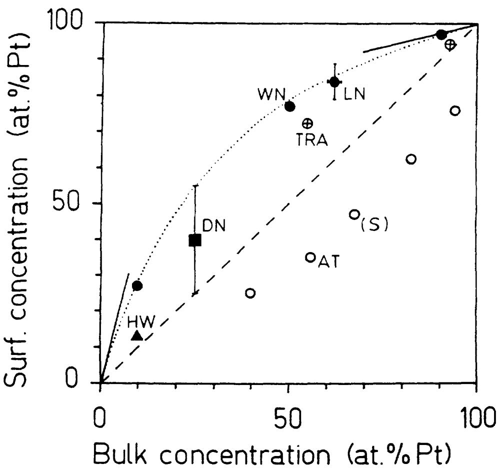


FIG. 11. Comparison of our data on the top layer composition of Pt-Rh alloys with those obtained by other techniques. Data points indicated by TRA are from Tsong, Ren, and Ahmad (the present study), LN is from Langenveld and Niemantsverdriet (Ref. 17), WN are from Williams and Nason (Ref. 14), DN is from van Deft and Nieuwenhuy (Ref. 16), and HW is from Holloway and Williams (Ref. 15). Data points AT are from Ahmad and Tsong (Ref. 5) obtained with samples containing sulfur impurities. All results with pure Pt-Rh alloys show that Pt segregates with only the amount varying. Sulfur definitely reverses the segregation behavior of Pt-Rh alloys.

B. Cosegregation of Pt-Rh and Pt-Ru alloys with sulfur

Grain boundary and interface segregation of impurities is one of the important subjects of research in physical metallurgy. Surface segregation of impurity atoms and cosegregation of impurities with alloy species is an important subject in applied surface science, as the physical and chemical properties of the alloy surfaces will be drastically changed by such segregation. Here we discuss cosegregation with sulfur for Pt-Rh and Pt-Ru alloys.

TABLE I. TOF atom-probe data for surface segregation of alloys.

Alloy systems	Segregating element TOF AP data	Theories[a]	Extent of segregation (atomic layer)	Nature of convergence to bulk value	Reference
Ni-Cu	Cu	Cu	1	Oscillatory	3
Fe–Cr–1 at. % Mn	Cr	Cr	1	?	31
Pt-Au	Au	Au	4	Monotonic	4
Pt-Rh	Pt	Pt	1	Oscillatory	This work
Pt-Ru	Pt	Pt	1	Oscillatory	This work
Pt-Rh-S	Rh		1	Oscillatory	5
Pt-Ru-S	Pt		1	Oscillatory	This work
Pt-Ir-S	Pt	Pt	2	Monotonic	5
Ni-Cu (annealed in N_2)	Cu		1	Strong plane edge effect	23
Ni-Cu (annealed in O_2)	Ni		many	Nickel oxide formation	23

[a] See Refs. 24–28.

TABLE II. Parameters in surface segregation of alloys (model by Mezey and Giber). Here $\delta_2^* = (r_1^0 - r_2^0)/r_2^0$, r_i^0 is the surface free energy of the pure component *i*; $\Delta r_2^* = (r_2 - r_1)/r_1$, r_i is the atomic radius of the component *i*.

Alloy system	δ_2^* (%)	Δr_2^* (%)	Predicted segregation species	Observed species
Pt-Rh	-5	-3	Pt	Pt
Pt-Ru	-21	-3	Pt	Pt
Pt-Ir	-17	-2	Pt	Pt
Pt-Au	$+65$	$+4$	Au	Au
Ni-Cu	$+22$	$+2$	Cu	Cu

Sulfur is known to be able to promote certain chemical reactions and to inhibit other chemical reactions. In this study we are specifically trying to answer the following questions. First, will impurity atoms segregate to the surface? And, second, will the impurity atoms change the segregation behavior of the alloy?

For Pt-Rh alloys, we have derived absolute composition depth profiles for five different bulk compositions. These alloys contain about 50 ppm or less of impurity sulfur. Upon annealing to 700 °C for 5 min, sulfur atoms segregate to the surface to form a chemisorbed overlayer. At the same time the segregation species at the top surface layer reverses to Rh, and the second layer is now enriched in Pt as shown in Fig. 7. Thus the surface segregation behavior of Pt-Rh alloys is completely reversed by the presence of less than 50 ppm of sulfur impurity atoms. It is also found that the concentration of Rh in the top surface layer is linearly proportional to the overlayer coverage of sulfur as shown in Fig. 8. As the areas sampled for the overlayer and the top layer are not exactly the same, it is difficult to say that each Rh atom is associated with one sulfur atom. However, from Fig. 8, it is very likely that this is actually the case. These data indicate that Rh atoms are drawn to the surface by sulfur atoms, and the driving force in this cosegregation is really the impurity atoms. The Rh—S bond in the alloy is much stronger than the Pt—S bond.

The data shown in Fig. 8 have another significance. We always have the question of whether alloys annealed under our experimental conditions have really achieved thermal equilibrium of the distribution of the alloy species. The fact that under such annealing of Pt-Rh alloys, with and without the presence of about 50 ppm of sulfur, the surface segregation behavior reverses completely indicates clearly that these alloys must have reached the thermodynamic equilibrium distribution of the constituent species. For alloys with a trace of S, the top surface layers are always depleted in Pt, the second layers are enriched in Pt and from the third layers on the compositions return to the bulk values, as shown in Fig. 9.

For a Pt-Ru alloy, however, we do not find such a reversed surface segregation behavior in the presence of sulfur impurities. When a Pt-17.7 at. % Ru with sulfur is annealed at 700 °C, we find an overlayer of sulfur of only about 0.1 monolayer, and the composition depth profile is almost identical to that obtained with the alloy sample with no sulfur impurities, as shown in Fig. 10. Thus for this particular alloy, the presence of a small amount of sulfur does not seem to change significantly the surface segregation behavior. This result indicates that in this alloy, Pt-S interaction is not significantly different from Ru-S interaction.

IV. CONCLUSIONS

Our result for the top surface layer concentration in Pt-Rh alloys is in good agreement with results obtained in many other studies of surface segregation using mostly AES. This can be seen in Fig. 11. However, our depth profiles contain subtle features which most macroscopic techniques cannot investigate. Not only we are able to observe a plane edge effect, we are also able to show how the segregant concentration approaches the bulk value. For some alloys surface segregation is confined to the top surface layer, while for others the enrichment of segregant may extend to a few layers. Also the segregant concentration may approach the bulk value monotonically or nonmonotonically. In Table I results of our TOF atom-probe studies are summarized together with predictions of surface segregation theories[24–26] for the segregation species. In Table II we list parameters and predictions of segregation species in all the alloys we have investigated so far using the simple criterion of Mazey and Giber.[27] It is clear that our experimental results agree with available theories of surface segregation quite well when the segregation species is the only concern. As far as we are aware, there has been no prediction of depth profiles for specific alloy systems. Barnett *et al.*[19] have shown that the segregant concentration can decay into the bulk value nonmonotonically. King and Donnelly[28] use a Monte Carlo method to find the composition depth profiles of some alloy systems, in good agreement with our result. Now that statistically reliable composition depth profiles are available from TOF atom-probe measurements, it is worthwhile for theorists to investigate in more detail dynamics of surface segregations for specific alloy systems.

In our studies we have also obtained composition depth profiles for impurity cosegregation of Pt-Rh and Pt-Ru alloys. Although impurity segregation and cosegregation to interfaces are common knowledge and there have been reports of such segregation to surfaces,[29,30] as far as we are aware, no composition depth profiles have been obtained before. We have observed a reversed surface segregation of Pt-Rh alloys due to the presence of sulfur impurities in the alloys, but not for Pt-Ru. Thus impurity cosegregation of alloys is also chemically specific. Finally, we believe that our composition depth profiles can be used as references for calibrating macroscopic surface analytical techniques.

ACKNOWLEDGMENTS

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