

Oscillatory compositional depth profiles in surface segregation of a Pt-Rh alloy

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Surface segregation of a Pt-Rh alloy is studied with the single-atom chemical analysis capability of the atom-probe field ion microscope. We find the composition of the near-surface layers of the {001} plane to oscillate with the depth of the atomic layers having the top layer enriched with Pt. This oscillatory feature persists down to a depth of over ten atomic layers. The amplitudes of the oscillations decrease with the annealing temperature. In contrast, for Pt-Rh alloys containing a small amount of sulfur, the top alloy layer is enriched with Rh but a similar oscillation exists.

The chemical distribution of a solid-solution alloy should be fairly uniform over the entire bulk of the sample. Near the surface, because of the breaking of the symmetry of the crystal, the uniform distribution of the alloy components may no longer represent the distribution of the lowest free energy of the system. The alloy components may redistribute in the near-surface layers, or surface segregation may occur. Surface segregation is the simplest form of interface segregation. It is an important issue in surface science, condensed-matter and materials science, and catalytic chemistry. In the past one focused on the questions of what are the segregation species in different alloys and what are the concentrations of these species at the surface, etc. Recent studies focused on the detailed composition-depth profiles, which should be a more complete information source for understanding the mechanisms and the dynamics of surface segregation.¹⁻⁵

There are three different known surface segregation behaviors. They are a monotonic decay into the bulk concentration of the segregated species, a long-distance oscillatory compositional variation in the near-surface layers, and an atomic-layer-by-atomic-layer oscillatory compositional variation in the near-surface layers. For solid solution alloys, if the pair interactions of homonuclear and heteronuclear pairs are sufficiently similar, a monotonic decay of the segregant concentration should be expected. The second behavior appears to be associated with the oscillatory and long-range nature of the electronic⁶ as well as the atomic interactions,⁷ whereas the last behavior seems to be associated with the short-range forces between the constituent atoms as well as with the order-disorder transformation of the alloys.^{8,9}

Earlier experimental and theoretical studies established the long-range nature and oscillation of segregants in some alloys.^{1,5,6} Recent direct time-of-flight (TOF) atom-probe compositional analyses provide evidence of an atomic-layer-by-atomic-layer compositional oscillation in surface segregation down to the depth of the third atomic layer for Pt-Rh and Pt-Ru alloys.² Gauthier *et al.*⁴ conclude from low-energy electron-diffraction (LEED) intensity analyses that in Pt-Ni alloys, an

atomic-layer-by-atomic-layer oscillatory surface segregation occurs down to a depth of three atomic layers. In surface cosegregation of Pt-Rh(S), atom-probe data show a similar behavior down to a depth of several atomic layers.³ As far as we are aware, there are as yet no data from direct compositional measurements on surface segregation of alloys showing an atomic-layer-by-atomic-layer compositional oscillation down to a depth beyond the third atomic layer. We present here atom-probe data showing unequivocally this compositional oscillation down to a depth of over ten atomic layers in Pt-44.8 at. %Rh alloy. In addition, these data also show clearly how the oscillational amplitude of each layer decreases with the annealing temperature. All these observed features are remarkably similar to those concluded from theoretical studies for Cu-Au and Pt-Ni alloys.^{8,9}

Experimental procedures of atom-probe mass analysis in surface segregation studies have been described in our earlier publications and will not be repeated here. In this experiment, sample tips are prepared from a high-purity Pt-Rh wire which is further treated by heating in high-purity oxygen to $\sim 1000^\circ\text{C}$ for several hours. Since both Pt and Rh are noble metals, this is a good way to remove impurities such as sulfur and carbon inside the wire. The wire is further heat treated in vacuum in low pressure (10^{-10} Torr) at $\sim 1000^\circ\text{C}$ for two to several hours. Tips are then polished from this wire using a standard method.¹⁰ Before a tip is used for an experimental measurement, it is carefully cleaned and degassed at $\sim 700\text{--}800^\circ\text{C}$ in UHV and then developed to near atomic perfection by field evaporation at ~ 30 K. It is then annealed to a specified temperature for several to over 30 minutes to equilibrate the distribution of alloy components and then quenched to ~ 30 K. The probe hole is aimed at the edge of the top surface layer and TOF atom-probe mass analysis by slow pulsed field evaporation is done. As the surface is slowly field evaporated, the tip orientation is gradually adjusted so that the probe hole is always aimed at the edge of the top surface layer. When the top surface layer is completely field evaporated, the second layer is analyzed by adjusting the probe hole to its edge. A geometrically realistic picture of the

volume sampled using this procedure can be found in Fig. 1 of Ref. 3. The tips used in this study usually have a radius of several hundred to near 1000 Å. After an annealing, the size of a low-index facet is usually about 100 Å or larger. The probe hole covers a circular area of about several to ~ 10 Å in diameter. For the top surface layer, the first few atoms collected come from the plane edges. From the second layer down, edge atoms are already field evaporated when the layer is analyzed; therefore, there is no edge effect. For Pt-Rh alloys, however, our earlier study already found the edge effect to be very small; it can be omitted without introducing an appreciable error.^{2(b)} As the number of atoms analyzed from a particular atomic layer is small, the experiment has to be repeated many times using identical conditions. Several sets of data are then combined according to the depth of these layers to render the data statistically reliable.

In using atom-probe mass analysis for the composition of a sample, one has to make sure that no preferential field evaporation of one species occurs. This question was answered for Pt-Rh alloys to be affirmative, as shown in Fig. 1 of Ref. 2(d). Another relevant question is whether the sample so prepared has reached thermodynamic equilibrium. This question has been answered experimentally for Pt-Rh alloys in our previous publications.^{2(a),(b)} We will explain briefly here. We find that as long as the annealing temperature is above 700°C,

an annealing time of 3–30 min does not give appreciable difference in the composition-depth profile. Within an annealing period, the root-mean-square displacement of a bulk atom is estimated to be between 30–100 Å when the temperature is changed from 700 to 1000°C. As the tip size is very small, thermodynamic equilibrium distribution can be achieved much more quickly through surface diffusion. Thus the time needed to achieve equilibrium distribution is much shorter for tips than that needed for macroscopic samples. While we are not certain that global thermodynamic equilibrium has been achieved in our samples, we are certain that at least local thermodynamic equilibrium has been reached. Thus annealing times of 3–30 min do not change the composition-depth profiles appreciably.

In Figs. 1(a) and 1(b), we show the cumulative numbers of ions detected from the {001} plane of one sample equilibrated at 975 K and one equilibrated at 1175 K. Only data collected from the first three atomic layers are shown. From the slopes of the line segments, one can easily see the oscillatory nature of the compositional variation. Figures 2(a)–2(c) show the absolute composition-depth profiles we have obtained for samples equilibrated at 975, 1075, and 1175 K. The 975-K data clearly exhibit a compositional oscillation down to the depth of the tenth atomic layer. For the 1175-K data, on the other hand, the oscillation can be seen only for three or four

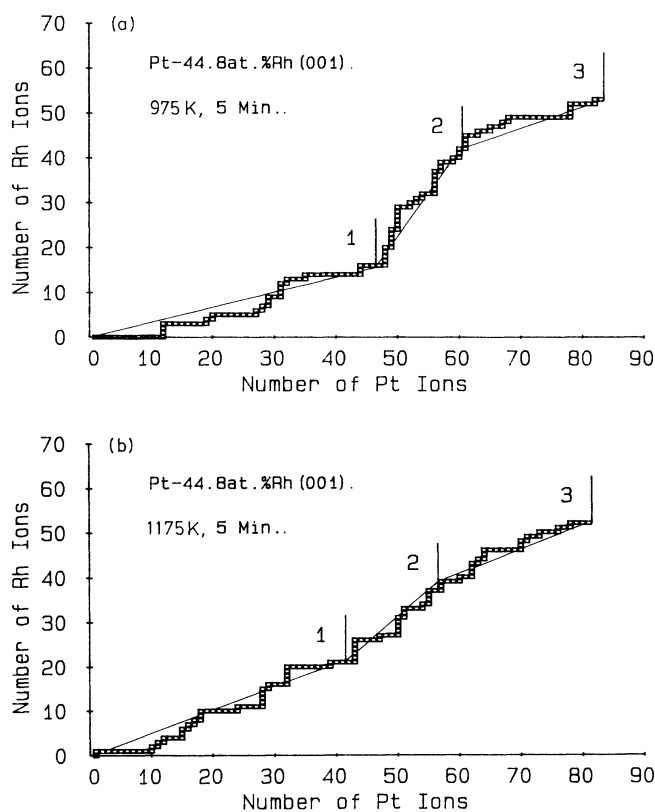


FIG. 1. (a) Cumulative plot of ions detected from the first three atomic layers of a sample annealed at 975 K. (b) A similar plot for a sample annealed at 1175 K.

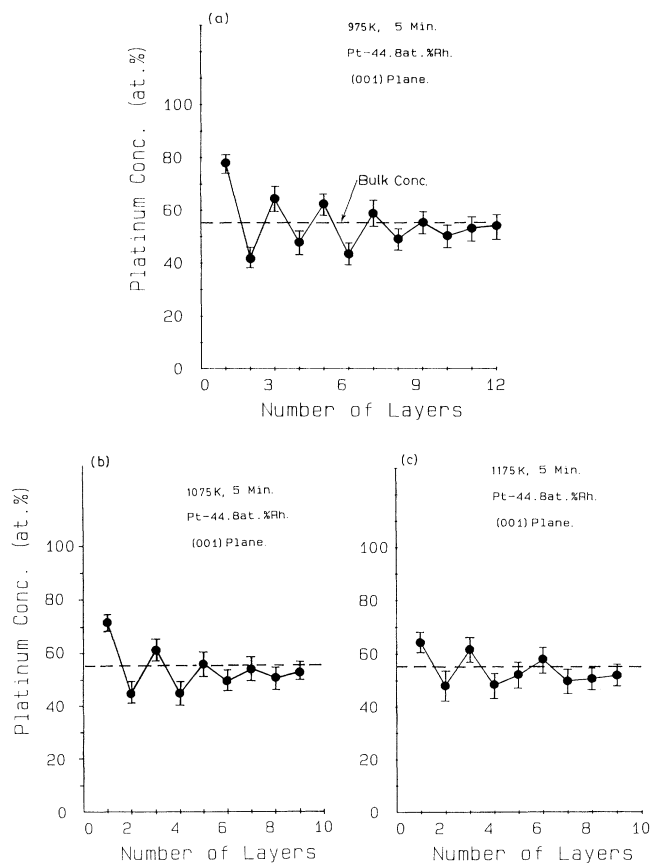


FIG. 2. Composition-depth profiles derived from samples equilibrated at (a) 975 K, (b) 1075 K, and (c) 1175 K.

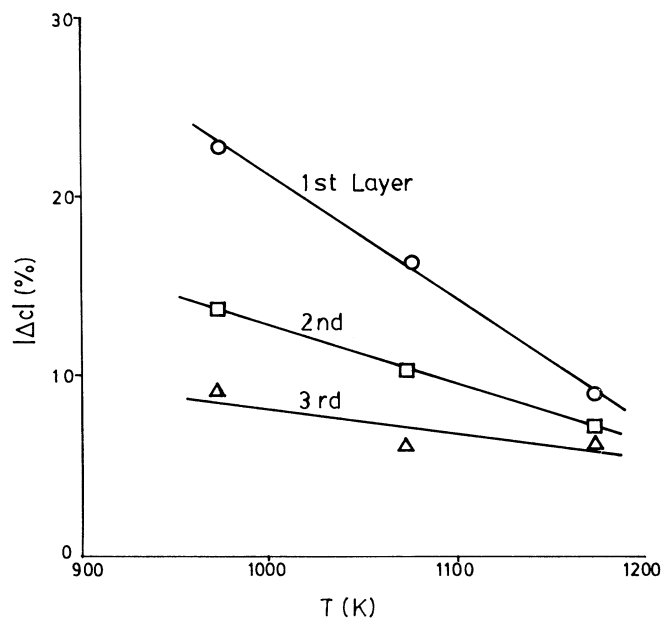


FIG. 3. The magnitude of Δc , which is the difference between the concentration of platinum of a near-surface atomic layer and that of bulk, as a function of the annealing temperature.

atomic layers. The amplitudes of these oscillations are found to decrease continuously with increasing annealing temperature, as shown in Fig. 3. These data also fit well into straight lines when they are plotted in Arrhenius form. Because of the tediousness of the atom-by-atom detection atom-probe experiment and the large statistical uncertainty in such type of data, it is not possible to find the functional form of the temperature dependence. However, all the features in these data are very similar to those theoretical results obtained for Cu-Au and Pt-Ni alloys.^{8,9}

For Cu-Au alloys, the atomic-layer-by-atomic-layer

surface segregation is believed to be associated with the order-disorder transformation of the alloys.⁸ For the equiatomic ordered phase of these alloys, the structure is the $L1_0$ type. Fundamental planes, such as the (001), have pure metal layers of the two components stacked in alternating sequence. Ordering may start from the near-surface layers where rearrangements of atoms should be easier. But even in these alloys, the association of the order-disorder transformation with surface segregation behavior is not completely transparent. In $L1_0$ structure, (100) and (010) are superlattice planes which are not equivalent to (001); here every layer is a 50:50 mixed layer. One should note also that Pt-Rh alloys are not ordered alloys. Neither are the systems we have studied stoichiometric. Thus the oscillation we have observed may be purely a surface segregation effect. We would like to mention that impurity segregation in a grain boundary behaves very similar to surface segregation, or it exhibits an oscillatory long-range profile also.¹¹ Here, again, no connection can be made with order-disorder transformation.

For comparison, we would like to point out here that for Pt-Rh(S) alloys containing less than 50 ppm of sulfur impurity, sulfur atoms will cosegregate to the surface. Although the composition of the near-surface layers also oscillates, the top metal layer is now enriched with Rh atoms, as can be seen in Fig. 2 of Ref. 3. In summary, our experiments have now established unequivocally the oscillatory nature of the compositional variation down to the depth of approximately the tenth atomic layer in surface segregation of Pt-Rh and cosegregation of Pt-Rh(S) alloys. The amplitude of the oscillation decreases with the annealing temperature as also found in the theoretical calculations. A trace of sulfur impurity in the alloy will induce a 180° phase shift in the oscillation of every layer in addition to the formation of an overlayer of sulfur at the surface.

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