

## Surface Compositions of Solid and Liquid Indium-Tin Alloys by Auger Electron Spectroscopy Using Ion Bombardment

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Equilibrium surface compositions of solid and liquid In-Sn alloys of various bulk compositions were examined by Auger electron spectroscopy. The compositional relaxation at the solid surfaces of this alloy system was very fast, and utilizing this the bulk compositions of the solid alloys and the corresponding surface compositions were determined using Xe-ion bombardment in conjunction. Above the temperature 1.2 times the melting point, the surface compositions were constant regardless of temperature, and coincided with the nominal bulk composition. As the temperature was lowered toward the melting point, surface segregation became apparent, and at around the melting point the surface composition nearly coincided with those of the solid alloys. When surface segregation occurred, In segregated to the surfaces of Sn-rich alloys and Sn to the surfaces of In-rich alloys. Under the influence of surface oxygen In segregates to the solid surface at any alloy composition. © 1986 Academic Press, Inc.

### Introduction

Metal alloys have been drawing the attention of catalyst researchers (1, 2), not only because alloying of two metals often results in catalytic properties very different from that of each component metal, but also because the study of alloy catalysts may provide us with an insight into the very nature of catalysis by metals. Catalytic activities of alloys are strongly influenced by their surface characteristics. Two distinctive effects of alloying are envisioned (2): The "ensemble" effect by which the number of catalytically active multiplet sites on the surface are altered, and the "ligand" effect by which the electronic properties of

the surface active sites are modified. While the study on the physical characteristics of alloy surfaces, such as surface compositions and surface electronic structures, is indispensable in understanding alloy catalysis, most of the studies on alloy surfaces have been concentrated on the class of group VIII-IB binary alloys (1, 3), and reports on other systems have been limited.

The present paper is concerned with the surface characterization of the one of those scarcely studied nontransition metal systems, In-Sn alloys. Indium is an active catalyst for the dehydrogenation of alcohols and tin is inactive (4). When these two metals are alloyed, we get butanol dehydrogenation activities that vary sigmoidally with respect to the bulk In concentration at

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the temperatures well above the melting point of the catalyst alloy (4).

The In-Sn alloy system does not give solid solutions except at very dilute ends. This poses a difficulty in measuring even a basic surface characteristics, such as the surface composition of the alloy in solid state, since the nominal bulk composition is not always the "bulk" composition directly below the surface on which such surface characteristics are being measured. Thus to date only the surface compositions of very dilute In-Sn solid solutions have been reported (5, 6).

There is another difficulty, as it turned out in the present study, inherent with this particular alloy system: very fast diffusional relaxation at the surface. This excludes the possibility of using an *in situ* fracturing device for the measurement of bulk compositions since during the sample aligning and focusing after the fracturing the composition of the fractured surface would deviate from the bulk value.

To circumvent these problems, we employed ion bombardment in conjunction with Auger electron spectroscopy (AES). Ion bombardment has been shown as a useful tool in examining solid surfaces (7, 8). The merit of the use of ion bombardment-AES is that both the ion gun and the electron energy analyzer may be kept focused at the same fixed spot on the sample surface (7). This enables one to monitor constantly the surface composition changes during and after the ion bombardment, and to determine uniquely the bulk and the corresponding surface compositions.

The present paper reports the surface compositions of solid In-Sn alloys over the entire range of bulk compositions thus determined. The effect of the presence of surface oxygen on the surface compositions is also examined. In view of the fact that the butanol dehydrogenation activity measurement has been made above the melting point of the alloy catalyst, an AES chamber

suitable for liquid sample handling is also constructed, and the surface compositions of the liquid alloys are measured.

## Experimental

Indium-tin alloys were prepared by the method described earlier (9), viz., melting high-purity indium (99.999%) and tin (99.999%) in a Pyrex tube under bubbling hydrogen. Alloy ingots thus prepared were cold-rolled to 0.8 mm thickness under the ambient atmosphere, annealed at 373 K for 5 hr under flowing hydrogen, then degreased by trichloroethane using an ultrasonic cleaner.

Bulk and surface compositions of solid alloys were measured by using a PHI model 545 SE scanning Auger spectrometer. Ion bombardment with  $7 \times 10^{-3}$  Pa of Xe at 2 kV accelerating voltage on the sample surface and its cessation were repeated, and the Auger peak-to-peak intensities of In (at 404 eV), Sn (430 eV), O (503 eV), and C (273 eV) during these cycles were recorded by a multiplexer. Sensitivity ratio of In/Sn is determined to be 1.0 from the liquid alloy AES measurement described below at high temperatures, where no surface segregation was observed.

For the surface composition measurements above the melting point, an ultra-high-vacuum chamber, shown in Fig. 1, with a vertically mounted Auger assembly (PHI model CMS-10-155) was constructed. Sample alloy was held horizontally in a Pyrex vessel and heated by a Ta wire heater from below. The sample is grounded by a W wire imbedded in the vessel. Sample temperature was measured by a thermocouple in contact with the vessel, and is calibrated by the melting point of each sample alloy. For the cleaning of the surface oxygen on the liquid samples Ar mixed with ca. 1% H<sub>2</sub> was employed as a sputtering gas. Argon alone was not sufficient to sputter-clean the surface oxygen above melting point.

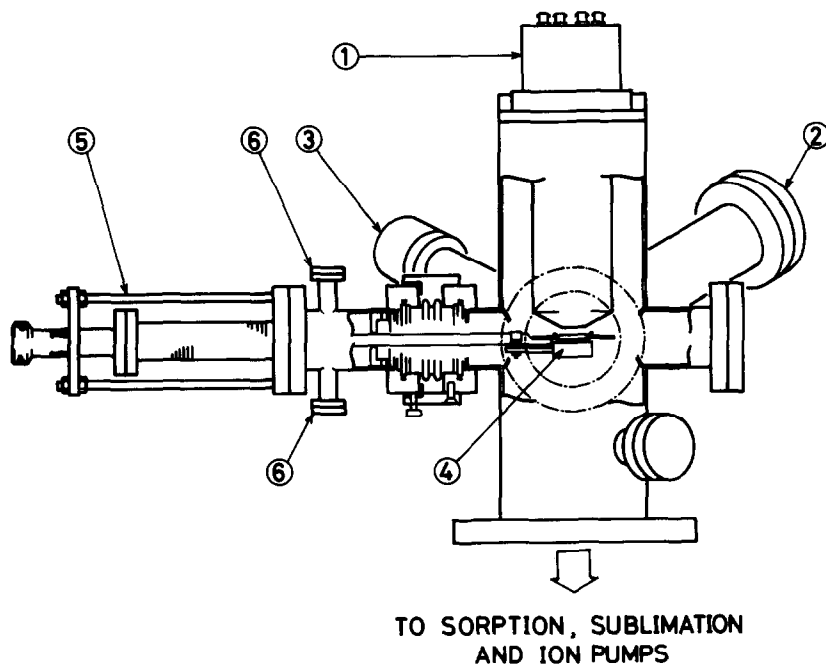


FIG. 1. Ultra-high-vacuum chamber for liquid AES measurements. 1, Auger assembly; 2, quadrupole mass spectrometer; 3, ion gun; 4, sample holder and heater; 5, manipulator; 6, electrical feed-through.

## Results and Discussion

### *Response of Solid Alloy Surface Compositions to Ion Bombardment*

Figure 2 shows a typical surface compositional changes of a solid sample during the cycles of Xe-ion bombardment and its cessation. Ion bombardment preferentially sputters In from the surface of this sample during the early stage of each bombardment period, quickly decreasing the In/Sn Auger intensity ratio to a steady-state value. When bombardment is stopped, the surface composition quickly relaxes back to its equilibrium value. Meanwhile surface contaminants (C, O) are progressively removed from the surface by the repetition of bombardment. Note that after the surface contaminants are entirely removed from the surface, response of In/Sn intensity ratio to the bombardment-relaxation cycle is com-

pletely reproducible for its repetition (compare the last two cycles in Fig. 2). This reproducibility, however, was not observed

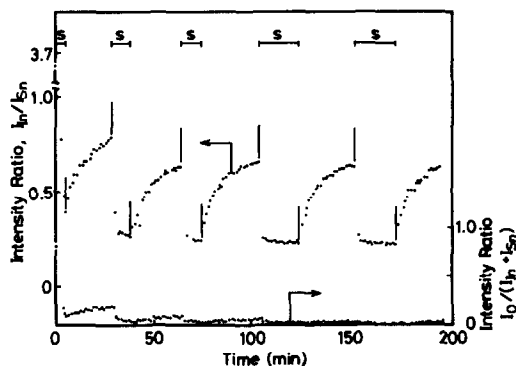


FIG. 2. Compositional changes of the surface of a solid In-Sn alloy during the cycles of Xe-ion sputtering and its cessation. Sputtering periods are indicated by *s* in the figure. Bulk In content: 20 at.% nominal.

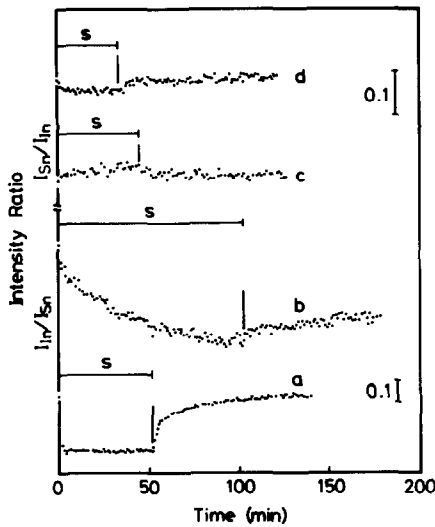


FIG. 3. Various response patterns of the solid alloy surface compositions to ion sputtering and the following relaxation. Sputtering period is denoted by *s*. Nominal bulk In content: a, 20%; b, 40%; c, 80%; d, 90% atomic.

for samples with nominal bulk compositions of around 50% (cf. Fig. 3).

Figure 3 compares the Auger intensity ratios of In and Sn for various samples during the last bombardment-relaxation cycle which is taken after the surface contaminants are completely removed. Three distinctive response patterns for the cycle were observed, depending on the nominal bulk compositions. The first pattern, characteristic of Sn-rich alloys (sample *a* in Fig. 3), shows pronounced depletion of In and very fast attainment of steady state surface composition upon ion bombardment. The surface composition quickly returns back to the initial equilibrium surface composition upon cessation of bombardment. The depletion of In by bombardment is consistent with the higher sputtering yield for In compared to that for Sn (5) (also see later). The observed reproducibility of the surface composition for the bombardment-relaxation cycles indicates the homogeneity

of the sample within the probe depth of the current experiment. The fast attainment of steady-state surface composition upon bombardment, and its quick return back to equilibrium value upon cessation of it, indicate very fast diffusion of In and Sn atoms in the surface region, and this is utilized for the determination of the diffusion coefficient of each element (10).

The second pattern, characteristic of In-rich alloys (samples *c* and *d* in Fig. 3), also shows fast attainment of steady-state surface composition upon bombardment, and quick return back to the equilibrium upon its cessation, although the extent of compositional changes is much smaller than those of the first pattern. Compared to the Sn-rich alloys, all of which showed depletion of In, some of these In-rich alloys show apparent depletion of Sn. This may be understood as the result of two opposing effects, viz., preferential sputtering of In that enriches the surface with Sn, and the pre-existing depth-concentration profile that increases In concentration as sputtering proceeds, which is a characteristic of the Sn-rich alloys as shown later.

In the third pattern, characteristic of alloys with nominal bulk compositions of around 50% (sample *b* in Fig. 3), In/Sn intensity ratio does not reach steady state during bombardment. This is an indication that the bulk composition is continuously changing with depth, most likely because the sample consists of more than one phase and also because their phase boundaries might be at different positions for surface layers and bulk. Thus the average bulk composition at the subsurface may not be the same before and after a cycle of bombardment, and so is the average surface compositions in equilibrium with the subsurface bulk compositions. Due to this difficulty, samples with ca. 50% nominal bulk compositions were not used for the determination of equilibrium surface compositions.

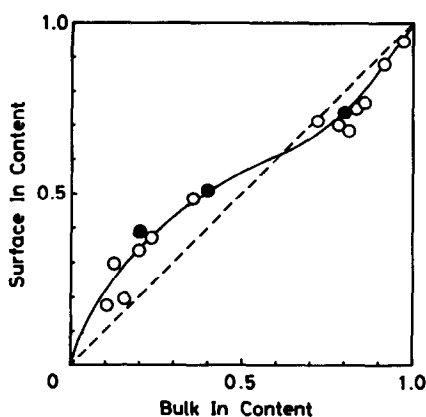


FIG. 4. Surface segregation in In-Sn alloys. Open circles, solid alloys; closed circles, liquid alloys at melting point.

#### *Equilibrium Surface Compositions of Solid In-Sn Alloys*

From the above bombardment-relaxation data, it is possible to deduce equilibrium surface compositions of In-Sn alloys at room temperature as a function of bulk composition. Bulk composition of each alloy sample was determined from the steady-state Auger intensity ratio under ion bombardment using the following equation (11):

$$C_{\text{In}}^{\text{B}}/C_{\text{Sn}}^{\text{B}} = (S_{\text{In}}/S_{\text{Sn}})(C_{\text{In}}^{\text{S}}/C_{\text{Sn}}^{\text{S}})$$

where  $C$  is the concentration of each component,  $S$  the sputtering yield, and super-script B and S denote bulk and surface, respectively. The quantity  $C_{\text{In}}^{\text{S}}/C_{\text{Sn}}^{\text{S}}$  is directly determinable from the Auger intensity ratio at the bombardment steady state. Sputtering yield ratio  $S_{\text{In}}/S_{\text{Sn}}$  may be taken to be equal to the ratio of surface binding energies of each component (12) since the atomic weight of In and Sn are almost the same to each other and the recoil energy densities may be taken constant for elements with atomic weight above 100 (13). Heat of mixing in In-Sn system is small

(14), and thus using the heat of vaporization of each component,  $S_{\text{In}}/S_{\text{Sn}}$  is evaluated to be 1.24. Multiplying these two quantities we obtain the bulk composition of each sample.

Equilibrium surface compositions for each samples were determined directly from the Auger intensity ratio taken after the bombarded surface has been relaxed. Compositional depth profile was not taken into account, and thus the surface compositions obtained here are in effect averaged over the escape depth of the Auger electrons. Considering the possibility that there may be bombardment-induced Gibbsian segregation in the subsurface (second) layer (12), the surface segregation thus obtained may be on the side of underestimating the extent of surface (first layer) segregation. In Fig. 4 the equilibrium surface compositions of solid alloys thus obtained are plotted (open circles) as a function of bulk composition. It is apparent that In-rich alloys segregate Sn to their surfaces and Sn-rich alloys segregate In. This is in agreement with the results of Frankenthal and Sinconolfi (6) who observed the same tendency for two dilute In-Sn solid solutions. The present experiment clearly establishes the nonregular solution behavior of the In-Sn system.

#### *Surface Compositions of Liquid In-Sn Alloys and Its Temperature Dependency*

Figure 5 shows the temperature dependency of the surface compositions of In-Sn alloys above their melting point,  $T_m$ . In the temperature range of  $T/T_m > 1.2$  the surface composition of each alloy showed constant value regardless the temperature, and it nearly coincided with the nominal bulk composition. This means that at this high-temperature regime surface segregation is nonexistent at the In-Sn alloy-vacuum interface within the accuracy of the present experiment. Previous estimation of the surface composition using the literature data of

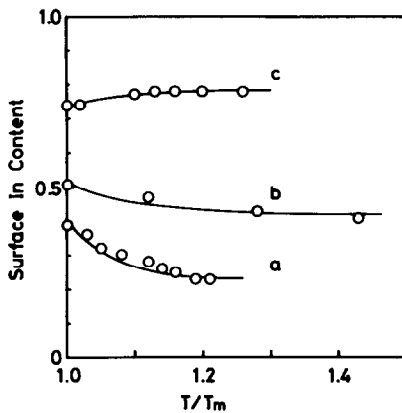


FIG. 5. The temperature dependence of the liquid alloy surface compositions. Nominal bulk In content: a, 20%; b, 40%; c, 80% atomic.

the surface tension measured at 623 K and activity coefficient at 773 K showed the occurrence of surface segregation at 523 K (15). Although the present experiment expects no surface segregation at 523 K which is much higher than  $T_m$  for most alloy composition, the similarity of the segregation tendency between the estimated and the present lower temperature data is noted.

When the temperature is lowered toward  $T_m$ , surface segregation becomes apparent as seen in Fig. 5, and is most prominent at around  $T_m$ . The surface composition at this point is plotted against the high-temperature surface composition (i.e., the bulk composition) in Fig. 4 (closed circles). The coincidence with the solid surface-bulk composition relation is noted.

#### Effect of Surface Oxygen on the Surface Composition of Solid Alloys

As is apparent in Fig. 2, surface compositional relaxation and attainment of its equilibrium are also observed in the earlier cycles of bombardment-relaxation, viz., even when oxygen is still present at the surfaces (see the first three cycles in the figure). These earlier equilibrations are apparently

under the influence of the oxygen present. Thus a plot of these equilibrium surface compositions versus bulk alloy compositions would yield an information on the effects of surface oxygen on surface segregation. Figure 6 shows such plot for two oxygen concentration levels. Since this experiment was not performed under controlled atmosphere, the amount of oxygen on the surface is not well fixed, and thus the results are only to show tendencies. Nevertheless, it is clear from the figure that the presence of surface oxygen enriches the alloy surfaces with In, and the higher the oxygen concentration the more pronounced the segregation.

Oxygen-induced or -enhanced segregation has been reported on numbers of alloy systems including Pt-Fe (2) and Pt-Sn (16). Such segregations are commonly interpreted in terms of the difference in the heats of oxide formation between the component metals: component with higher heat of oxide formation,  $-\Delta H_f$ , segregates to the surface. The present result is also consistent with this interpretation: the segregated component, In, has heat of  $\text{In}_2\text{O}_3$  formation of 466 KJ/mol In, which is much

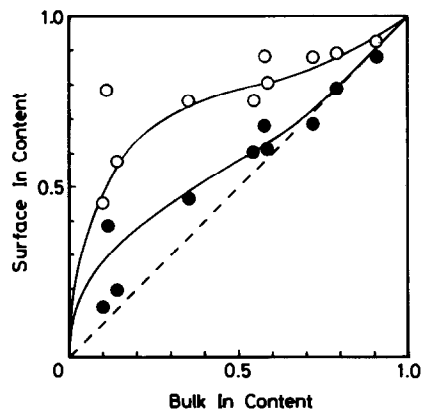


FIG. 6. Surface segregation in solid In-Sn alloys under the influence of surface oxygen. Surface oxygen content: open circles, 0.5-0.9; closed circles, 0.01-0.03 atomic.

higher than that of SnO which is 286 KJ/mol Sn.

The above result has significant implications for the interpretations of alloy catalysis. Most of the ultra-high-vacuum techniques for surface composition measurements, such as AES, XPS, and SIMS, measure the alloy surface compositions at the alloy-vacuum interface. Catalysis, however, takes place at alloy-reactant gas interface. Thus if alloy surface composition under vacuum is significantly different from that under reactant gas atmosphere, comparisons between the catalytic activity data with the alloy surface compositions obtained under UHV conditions may mislead the interpretation of the effects of alloying on catalysis.

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