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THE SURFACE STRUCTURE AND COMPOSITION OF THE LOW INDEX SINGLE CRYSTAL FACES OF THE ORDERED ALLOY Pt_3Sn

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The surface composition and structure of ⟨111⟩, ⟨100⟩, and ⟨110⟩ oriented single crystals of the ordered alloy Pt_3Sn (Ll_2 or Cu_3Au-type) were determined using the combination of low energy electron diffraction (LEED) and low energy ion scattering spectroscopy (LEISS). The clean annealed surfaces displayed LEED patterns and Sn/Pt LEISS intensity ratios consistent with the surface structures expected for bulk termination. In the case of the ⟨100⟩ and ⟨110⟩ crystals, preferential termination in the mixed (50% Sn) layer was indicated, suggesting this termination to be the consequence of a thermodynamic preference for tin to be at the surface.

1. Introduction

Pt-Sn alloys are of considerable commercial interest as both heterogeneous catalysts for hydrocarbon conversion [1,2] and as electrocatalysts for the direct electro-oxidation of methanol in fuel cells [3,4]. Because surface composition is critical to the behavior of alloys in these applications, there has been considerable study of the surface segregation phenomena in this system, both experimentally and theoretically. Of particular fundamental interest is the behavior of the highly ordered exothermic alloy Pt_3Sn, the alloy treated in one of the first theoretical analyses of segregation in ordered alloys [5]. Experimental studies of polycrystalline Pt_3Sn by Biloen and co-workers [6–8] found surface enrichment in Sn by LEISS, with surface compositions as high as 50–60 at.% Sn. However, in the theoretical analysis of Pt_3Sn by Van Santen and Sachtler [5], *no* segregation was predicted on the (111) face of the ordered alloy, and segregation was predicted on the (200) face by interchange of Pt atoms in the surface with tin atoms in the layer below to form a 50% Sn surface. To date we are not aware of any experimental study of the surface structure and composition of a Pt_3Sn single crystal, which would provide a more rigorous test of this segregation theory. In this paper, we communicate selected results from the first study of the surface structure and composition of the three low index single crystals of Pt_3Sn using a combination of low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and low energy ion scattering spectroscopy (LEISS).

2. Experimental

Single crystal Pt_3Sn was prepared by combining high purity platinum and tin in stoichiometric amounts and then refining the alloy using the Bridgeman-Stockberger technique under a helium atomosphere and in high purity alumina crucibles. Single crystal slices (1 mm × 10 mm diameter) were spark cut and mechanically polished down to 0.05 μm. All single crystal faces were within 0.5° of their respective crystal planes as determined by Laue back-reflection X-ray diffraction. LEED patterns were observed with 4-grid LEED optics (Varian) and AES spectra were recorded with a single-pass CMA (Varian). LEISS was conducted in another vacuum chamber equipped with a hemispherical analyzer (Leybold Heraeus). One keV Ne^+ ions were used for LEISS ($\varphi = 135°$) with variation of incidence angle from normal to 15° glancing. The beam current was 70 nA and the beam was rastered over a 3 mm × 3 mm area. Due to experimental constraints, no LEISS experiments were conducted with a variable azimuthal angle. The surfaces were prepared with cycles of Ar^+ sputtering, heating to 1023 K for 10 mins., approximately 10 L dosing of O_2 (at 5×10^{-8} Torr) at 623 K to remove carbon, followed by another vacuum anneal at temperatures up to 1023 K. Further experimental details are described elsewhere [9].

3. Results and discussion

In the Pt_3Sn structure ($L1_2$ or Cu_3Au-type) shown in fig. 1, the {111} planes are all equivalent and have the bulk composition, while the {100} and {110} planes alternate between 50% Sn:50% Pt and 100% Pt, resulting in two inequivalent regular terminations of the bulk crystal. These two terminations will be designated the (100) and (200) planes or (110) and (220) planes, respectively. If the three low index surfaces have bulk termination surface structures, as shown in fig. 1, then we would expect to see (100)-p(2 × 2), (100)-c(2 × 2), and (110)-(2 × 1) superlattice LEED patterns.

A poorly ordered (111)-(1 × 1) pattern was observed immediately after the initial ion bombardment of the ⟨111⟩ crystal. Analysis of the surface by Auger

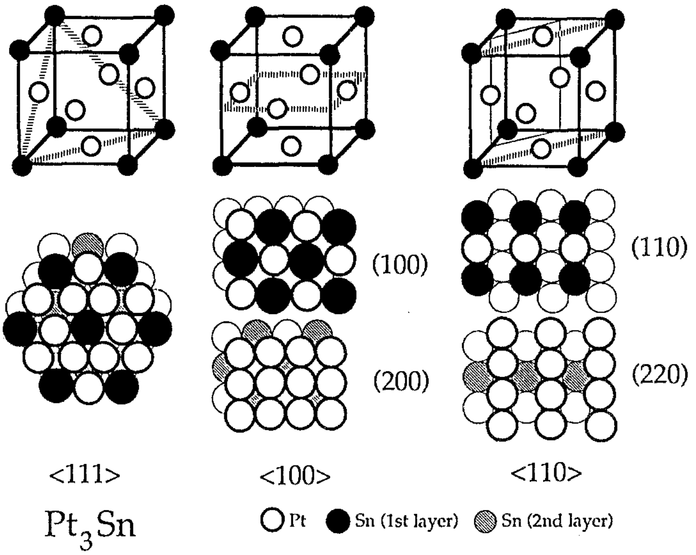

Fig. 1. Models for the structure of the three low index planes of Pt_3Sn formed by ideal truncation of the bulk $L1_2$ crystal.

electron spectroscopy showed that ion bombardment selectively sputtered tin from the surface, so that the bombarded surface has less than one-half of the stoichiometric amount of Sn. Subsequent thermal annealing restored tin to the surface and concurrently produced half-order spots in the LEED pattern, eventually forming a well-contrasted p(2 × 2) pattern [9]. Auger analysis showed that the Sn/Pt signal ratio stabilized when the annealing temperature was greater than 900 K. Carbon appeared on the surface during the initial anneal and was easily removed by oxygen dosing. Thereafter, the surface remained clean at all temperatures for extended periods of time. Once the clean annealed surface was formed, neither the LEED pattern nor the AES spectrum changed with temperature cycling between 300–973 K. The observed p(2 × 2) LEED pattern is similar to that observed on the ⟨111⟩ orientations of Cu_3Au [10–11], Pt_3Ti [12], and Ni_3Al [13], all three alloys having the same $L1_2$ structure as Pt_3Sn. It has also been observed on Sn vapor deposited on Pt(111) at a substrate temperature above 450 K [14].

The LEED patterns for Pt_3Sn ⟨100⟩ immediately following Ar^+ ion bombardment was also a poorly ordered (100)-(1 × 1), again associated with a low Sn/Pt AES ratio due to the preferential sputtering of tin. Upon annealing, the Sn/Pt AES ratio increased, eventually stabilizing to a ratio approximately 1.4 times that for the ⟨111⟩ crystal, and concurrently a c(2 × 2) LEED pattern appeared with characteristic streaking (actually fine structure) around the fundamental beams. Spot profile analysis [15] of the variation in the fine structure of the (10) and (11) beams with beam energy revealed the origin of the streaks. Using the same

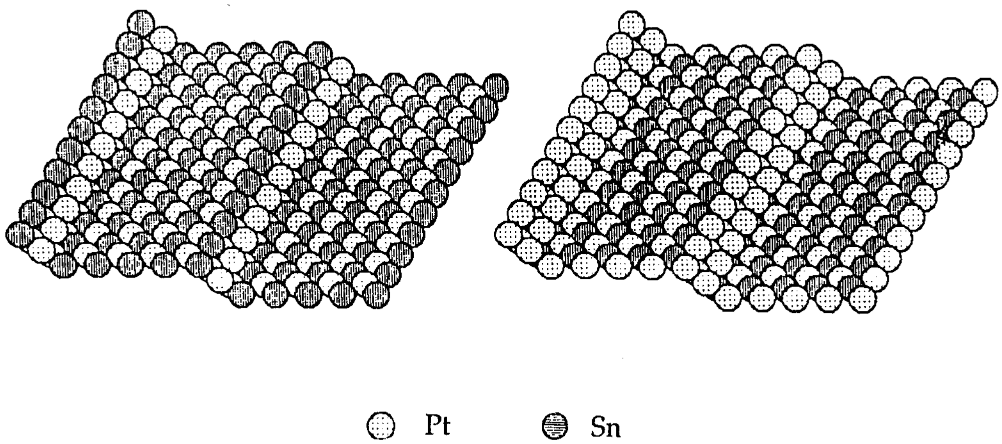

Fig. 2. Model of a step-terrace structure for the c(2×2) domains on partially annealed ⟨100⟩ Pt_3Sn. Terraces of (100) planes (50% Sn) are connected by diatomic steps, with the two possible atomic configurations along the step shown. On a larger scale, step edges are randomly perpendicular to one another and randomly up and down.

kinematic analysis we used previously for steps on pure Pt(100) surfaces [16], we determined that the step height was diatomic and the streaks arise from ordered step arrays, with the steps running preferentially along the (11) rows of the (100) surface. This means that the ⟨100⟩ crystal, in this partially annealed state, was preferentially terminated in c(2 × 2) terraces with alternating randomly up and down diatomic steps. A real-space model of such a step-terrace structure is shown in fig. 2. Annealing decreased the step density and increased the terrace length, eventually producing a reasonably flat surface with c(2 × 2) symmetry. A c(2 × 2) pattern (without streaking) was observed on the ⟨100⟩ crystals of Cu_3Au [10,11,17], Pt_3Ti [12], and Ni_3Al [18], all three alloys having the same $L1_2$ structure as Pt_3Sn.

The LEED pattern from the ⟨110⟩ crystal immediately after ion bombardment was a poorly ordered (110)-(1 × 2), indicative of a partially reconstructed [19] nearly pure Pt surface. During annealing and oxygen dosing, an unusual reconstruction of the surface was observed, which we have described in detail elsewhere [20]. This reconstruction was unstable, and after repeated cycles of ion-bombardment, oxygen dosing (to remove carbon) and annealing a sharp well-constrasted (110)-(2 × 1) was observed. As with the (111)-p(2 × 2) and (100)-c(2 × 2), once the pattern was formed, it was unaffected by thermal cycling, and observed at all temperatures between 300–900 K. The final equilibrium Sn/Pt AES ratio was approximately the same as that for the ⟨100⟩ crystal.

Random or aperiodic substitution of Sn for Pt atoms in the surface region is precluded by the observations of sharp superlattice LEED patterns. The superlattice patterns have the same symmetry as the bulk crystal, so it is reasonable to conclude that the low index surfaces have the same Sn substitution as in the bulk.

However, LEED patterns alone do not allow a distinction to be made between bulk termination in (100) in versus (200) planes, or in (110) versus (220) planes, since the back-scattering of low energy electrons in metals comes from several

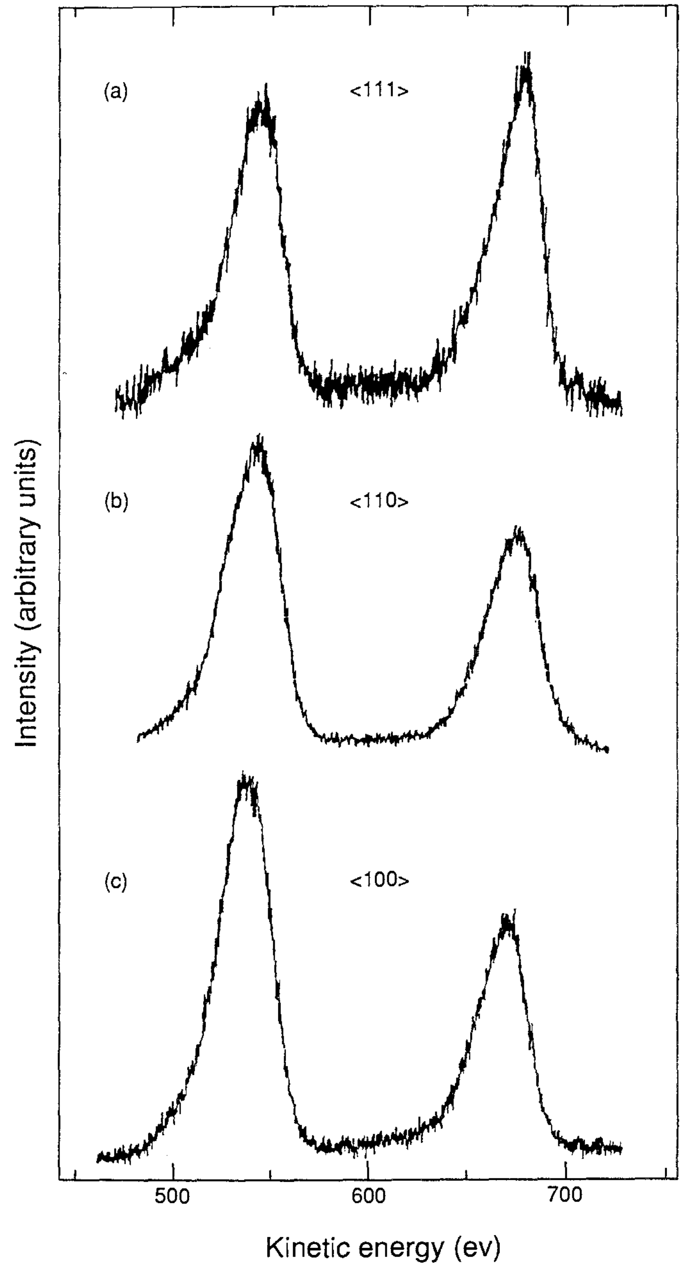

Fig. 3. Normal incidence Ne^+ ion scattering spectra for the clean annealed low index surfaces of Pt_3Sn. $E_p = 1$ keV, $\varphi = 135°$. The peak at 670 eV is scattering from Pt atoms, while the peak at 540 eV is scattering from Sn atoms.

atomic layers. Likewise, Auger spectroscopy does not permit a clear distinction to be made for the same reason. However, because of the very strong ion neutralization cross-section in metals [21], LEISS *is* capable of distinguishing, based on surface composition, between the three possible types of bulk termination: a.) an equal mixture of (100) and (200) planes, resulting in a surface composition equal to the bulk; (b.) preferential termination in the (100) plane, which produces a 50% Sn surface; (c.) or preferential termination in (200) plane, which produces a pure Pt surface.

The normal incidence LEIS spectra for the three clean annealed single crystals are shown in fig. 3. Using the theoretical ion-scattering cross-sections [21] for Sn and Pt, the normal incidence spectra indicate the surface composition of the ⟨100⟩ and ⟨110⟩ crystals is between 50–60% Sn, which clearly distinguishes preferential termination of these crystals in the compositionally mixed (100) and (110) planes versus the pure Pt (200) and (220) planes. A strong variation of the Sn/Pt LEIS intensity ratio with incidence angle was also observed, which indicates [9] that the Sn atoms are displaced outward from the plane of Pt atoms, similar to the displacement of Al atoms from the plane of Ni atoms in Ni_3Al [13,18]. This displacement was different for each crystal face, and this complicates quantitative analysis of the LEISS data. The most important phenomenon in this regard appears to be blocking of ions scattered from Pt atoms by the outwardly displaced Sn atoms in our scattering geometry ($\varphi = 135°$). This effect appeared to be most pronounced on the (111) surface, and caused the apparent Sn/Pt LEISS intensity ratio to be larger than expected for a 3:1 surface.

4. Conclusion

The ⟨111⟩ and ⟨100⟩ oriented single crystals have clean annealed surface structures that are closely related to the ideal bulk truncation structures. Some buckling in both surfaces is indicated by the angular dependance of the LEIS spectra, qualitatively similar to the buckling observed on Ni_3Al [13,18]. There is no evidence from the result with the ⟨111⟩ Pt_3Sn single crystal of surface segregation, a result correctly predicted by the Van Santen and Sachtler theory [5]. This theory also shows that the preferential termination of the ⟨100⟩ and ⟨110⟩ crystals in the compositionally mixed layers is the result of surface segregation constrained by strong ordering forces that prohibit the formation of either surface or subsurface layers not having the bulk substitution of the solute atom. Thus, it appears likely that the surface enrichment observed with polycrystalline Pt_3Sn [6–8] was due entirely to preferential termination in (100) and (110) planes (50% Sn) and not to the formation of surface planes that are not planes of the $L1_2$ structure, e.g. a (111) plane with 50% Sn.

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