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(510) SINGLE CRYSTAL SURFACE

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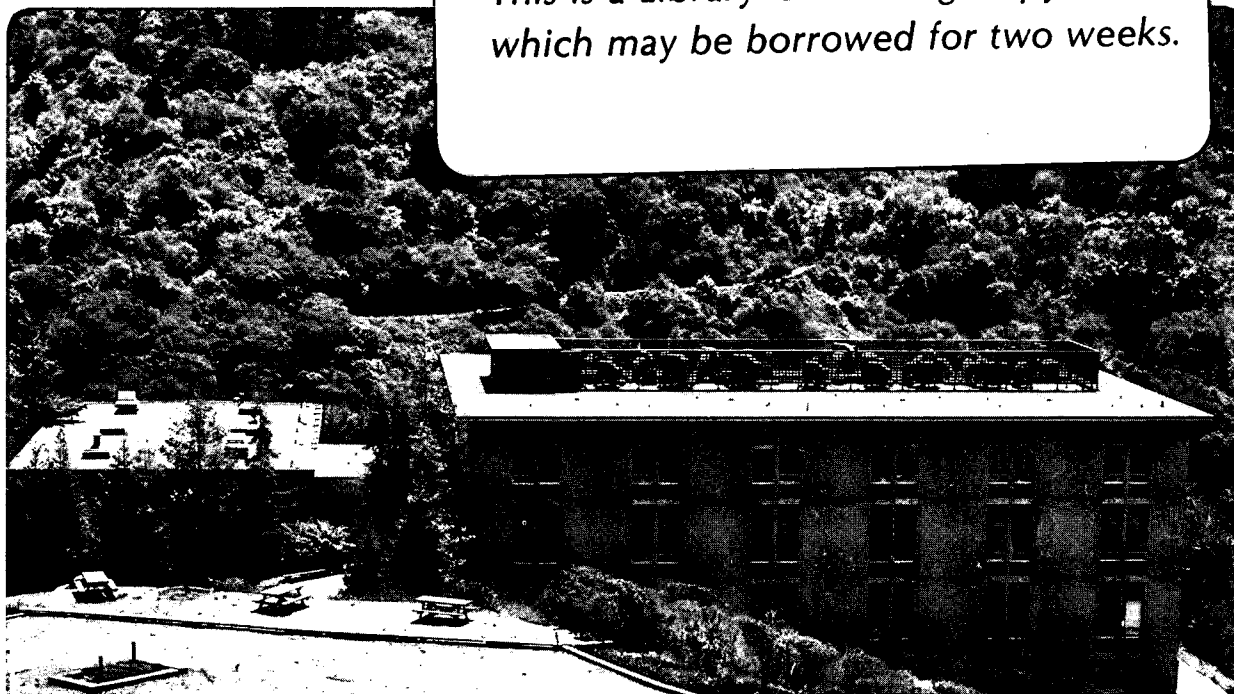
### Initial Stages of Oxidation of Binary Alloys: The Case of the Stepped Pt<sub>3</sub>Ti (510) Single Crystal Surface

U. Bardi, P.N. Ross, and G. Rovida

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INITIAL STAGES OF OXIDATION OF BINARY ALLOYS:  
THE CASE OF THE STEPPED Pt<sub>3</sub>Ti (510) SINGLE CRYSTAL SURFACE

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INITIAL STAGES OF OXIDATION OF BINARY ALLOYS:  
THE CASE OF THE STEPPED Pt<sub>3</sub>Ti (510) SINGLE CRYSTAL SURFACE

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ABSTRACT

The oxidation of the (510) oriented surface of the ordered fcc Pt<sub>3</sub>Ti alloy was studied by Low Energy Electron Diffraction and other surface sensitive techniques. The clean Pt<sub>3</sub>Ti (510) surface showed an ordered array of surface steps. Exposing the surface to oxygen at pressures in the range from  $1 \times 10^{-7}$  torr to  $1 \times 10^{-5}$  torr at temperatures of 800 K or higher caused the formation of titanium oxide islands on the surface. This process caused the progressive disappearance of the ordered array of steps, which was replaced by large facets oriented along the (100) and (210) planes.

The interest in the properties of a metal or alloy surface covered fully, or in part, by an oxide layer of thickness of the order of one atomic layer derives, among other factors, from the relation of such a surface to that formed on certain supported metal catalysts. It is generally believed that oxide islands, formed by migration of oxide moieties from the support material onto the surface of the metal particles, are related to the SMSI effect (Strong Metal to Support Interaction) [1,2]. In the case of alloy particles, oxide islands may also form on the surface as the result of oxidation and segregation to the surface of the more electropositive component. Besides the simple blocking of part of the active surface, such islands may affect the properties of the metal in a number of ways. In particular, the density of surface defects (such as steps) on the metal particles may be modified by the change in relative stability of different crystallographic planes due to the presence of oxide islands or the effect of preferential coverage of defects by the oxide islands.

The interaction of oxide islands with surface defects can be studied by surface sensitive techniques on single crystal "model" systems, where a regular array of surface steps can be created by cutting the surface along a high Miller index plane [3,4]. Although a number of studies have been reported on the oxidation of stepped metal surfaces [4,5], to our knowledge, no study has been performed so far on the oxidation of the stepped surface of a binary alloy. In the present work, which is part of a research program on the surface properties of platinum alloys [6-11], we studied the oxidation of the (510) oriented surface of Pt<sub>3</sub>Ti, which was found in a previous work [6] to show an ordered array of surface steps. We again used LEED and retarding-field AES, and in addition used XPS and Low Energy Ion Scattering Spectroscopy (LEISS) in another vacuum system equipped with a hemispherical analyser for electron and ion detection.

Cleaning of the Pt<sub>3</sub>Ti (510) sample surface after introduction in the vacuum system could be obtained by a treatment based on cycles of ion bombardment followed by annealing at or over 800 K. The LEED results relative to the clean Pt<sub>3</sub>Ti (510) surface have been reported in detail elsewhere [6] and will be shortly summarized here. The LEED pattern showed the "doublets" characteristic of an ordered array of surface steps [3,4] and the surface unit mesh was found to correspond to that expected for bulk truncation along the (510) plane. A model of the surface structure based on bulk truncation was

derived assuming a step height corresponding to two atomic rows and terraces of homogeneous composition.

After exposing the a Pt<sub>3</sub>Ti (510) surface to oxygen at pressure from  $1 \times 10^{-7}$  torr up to  $1 \times 10^{-5}$  torr at a temperature of 800 K or higher, we observed an increase of the relative intensity of the titanium and oxygen AES and XPS peaks, indicating surface precipitation of a titanium oxide. Examination of the Ti 2p XPS emission region indicated TiO<sub>2</sub> was the phase forming the overlayer upon oxidation at the pressures of the order of  $1 \times 10^{-5}$  torr. However, the oxide phases formed upon oxidation at lower pressure or after thermal treatment of the TiO<sub>2</sub> overlayer were found to be titanium in a lower oxidation state than in TiO<sub>2</sub>, most probably a defect "TiO" type phase. In general, the AES and XPS results for the Pt<sub>3</sub>Ti (510) surface after exposure to oxygen did not differ significantly from what previously observed for the (111), (100) and polycrystalline Pt<sub>3</sub>Ti (510) surfaces [8,16].

The results of CO thermal desorption tests are shown in Fig. 1. We found that the intensity of the CO desorption peak was reduced upon formation of titanium oxide on the surface. However, the shape of the peak remained qualitatively the same. The progressive increase in the amount of surface oxide led eventually to the complete suppression of CO chemisorption, as shown by curve 3 of Fig. 1. LEISS examination of such a surface with 1 KeV He<sup>+</sup> ions showed the disappearance of the Pt signal, indicating the complete coverage of the metallic surface by a layer of titanium oxide. In general, the LEISS results for the Pt<sub>3</sub>Ti (510) surface were similar to those reported in [16] for the Pt<sub>3</sub>Ti (100) surface.

The formation of islands of oxidized titanium upon oxidation was evidenced also by the formation of LEED superlattice patterns. All LEED results reported in the present work refer to oxidation in a range of pressure and temperature leading to the formation of titanium oxide with titanium in a lower oxidation state than in TiO<sub>2</sub>, as indicated by the XPS data. The LEED superlattice patterns on the Pt<sub>3</sub>Ti (510) surface were found to be the same observed on the Pt<sub>3</sub>Ti (100) surface in a previous study [8], where these patterns have been described in detail. These LEED results were interpreted in [8] as indicating the formation of flat titanium oxide islands of thickness of the order of one atomic layer and stoichiometry close to "TiO."

Upon gradual oxidation of the Pt<sub>3</sub>Ti (510) surface, in addition to the superlattice patterns due to the ordered oxide island, we also observed the following modifications in the substrate LEED pattern. The doublets corresponding to the ordered Pt<sub>3</sub>Ti alloy unit mesh disappeared, so that the substrate unit mesh became gradually that of a simple Pt (100) (1 × 1) surface. This process (observed also for the low index Pt<sub>3</sub>Ti surfaces [8]), can be interpreted as the progressive lowering of the titanium content of the subsurface layers upon titanium oxide segregation onto the surface. Facetting features (multiple specular beams) appeared in the pattern as weak, but sharp, spots, indicating formation of well-ordered domains larger than the coherence length of the LEED beam. Measurement of the angle of reflection of specular beams with respect to the surface normal indicated the reflection angle was  $52 \pm 2$  degrees along the [010] direction with respect to the normal to the (100) plane. Facetting features originated therefore from (210) planes (these planes form an angle of 26.56 degrees with respect to the (100) plane). The weakness of the (210) pattern did not permit a detailed interpretation, but the pattern appeared much more complex than what was expected from a simple bulk truncation of the Pt<sub>3</sub>Ti (210) surface. Therefore it appears that the (210) facets that form are already covered with a layer of titanium oxide. We also observed by LEED disappearance of the ordered step array and facetting when a graphitic layer was formed by ethylene adsorption and subsequent thermal treatment in vacuum.

Our LEED results, combined with the AES and XPS data and with the titration of the adsorption sites by carbon monoxide, present a reasonably detailed picture of the process of oxidation of the Pt<sub>3</sub>Ti (510) surface. In particular, the behavior of the "shoulder" feature in the CO thermal desorption spectrum enables us to draw some conclusions about the early stages of nucleation of the oxide film. The shoulder does not appear in CO TDS from low index Pt<sub>3</sub>Ti surfaces and was therefore attributed [6] to CO adsorbed on or near the step edges, whereas the main peak is related to CO adsorbed on the (100) terraces, since no change in the CO TDS peak shape was observed for the partially oxide covered Pt<sub>3</sub>Ti (111) and (100) faces [8]. Therefore, if the oxide grew preferentially along the step edges, the shoulder would be expected to disappear before the main peak for progressively higher oxide coverages. Instead, it is clear from the results of Fig. 1 that the shoulder is



not preferentially attenuated for a partial coverage of the surface with titanium oxide. Even though it is possible that some of the initial nucleation of the oxide occurs at the step edges, it appears that the primary growth of the oxide islands occurs simultaneously with the formation of large (100) and (210) facets of the metal substrate.

The results for the Pt<sub>3</sub>Ti (510) surface can be compared to those for pure Pt surfaces. Several detailed studies have been carried out on the interaction of platinum with oxygen, both on small particles [17] and on single crystal flat or stepped surfaces [4,5,18]. In many cases, clean Pt surfaces cut along high Miller indexes were found to form stable ordered step arrays. These stepped surfaces were found to restructure and facet upon exposure to oxygen. In the case of the Pt(510) surface, it was found [5] that the ordered step array is not stable, and that the clean surface restructures to form (210) and (100) oriented facets. It was also found [5] that the orientation of these facets did not change upon exposure to oxygen. The (100) and (210) facets are the same planes which were found in the present work to be the stable faceted surface for the oxidized Pt<sub>3</sub>Ti (510) surface. In general, the factor which stabilizes large facets vs. an ordered step array appears to be the variation in the relative surface energy of different crystal faces which occurs, for pure Pt, upon oxygen chemisorption [4,5] and, for Pt<sub>3</sub>Ti, upon formation of a layer of titanium oxide. However, as discussed in [6], factors related to the stability of the so called "quasi-hexagonal" reconstruction [19] of the Pt(100) plane also appear to destabilize ordered step arrays for the clean Pt(510) surface. Surface reconstruction was not observed for the Pt<sub>3</sub>Ti (100) surface [10], so that this factor does not affect the formation of an ordered step array on the Pt<sub>3</sub>Ti (510) surface.

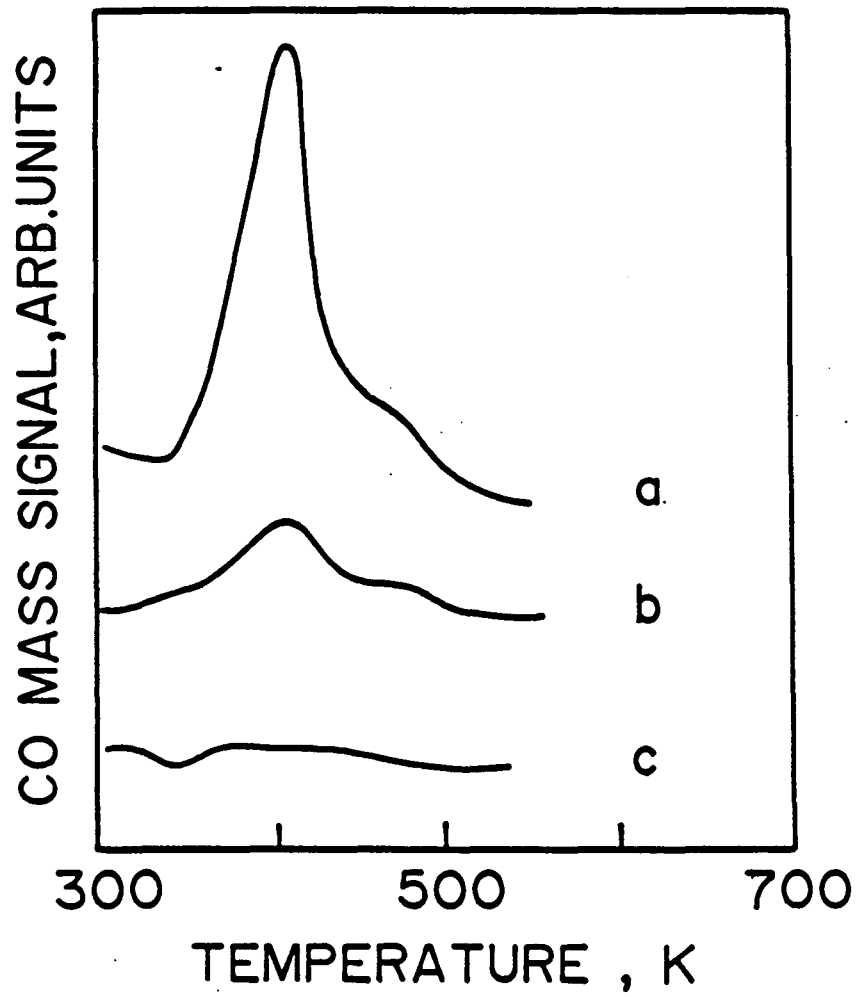
In conclusion, even though the structure and stability of the clean Pt(510) and ad Pt<sub>3</sub>Ti (510) surfaces differ, since the former facets while the latter forms a stable array of steps, upon oxidation the Pt<sub>3</sub>Ti (510) surface forms facets of the same crystallographic orientation as those shown by the Pt(510) surface.

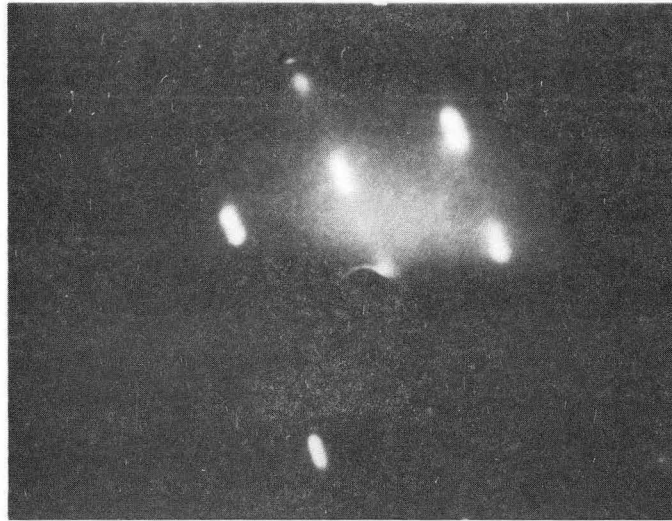
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## FIGURE CAPTIONS

1. Carbon monoxide thermal desorption spectra from the Pt<sub>3</sub>Ti (510) surface for different coverages of titanium oxide. CO exposure: 20 Langmuir at  $p = 5 \times 10^{-7}$  torr. Annealing speed: 22 degs/sec. A): Clean surface (No titanium oxide), B) partially oxide covered surface, C) completely oxide covered surface.
2. Evolution of the LEED pattern for successive exposures of the clean Pt<sub>3</sub>Ti (510) surface to oxygen at high temperature. All pictures were taken at the same electron accelerating voltage (86.5 V). A) Clean Pt<sub>3</sub>Ti (510) surface; Sharp doublets indicate the presence of a regular step-terrace array. B) After exposure to oxygen at  $p = 2 \times 10^{-7}$  torr for 5 minutes at 790 K: The new spots detectable are due to the formation of islands of oxidized titanium on the surface. Doublets are barely detectable. C) After exposure to oxygen at  $2 \times 10^{-6}$  torr for 5 minutes at 790 K. Doublets have totally disappeared.
3. Schematic representation of the effect of oxidation on the structure of the Pt<sub>3</sub>Ti(510) surface. A) Clean surface, showing an ordered array of steps and terraces. B) Oxidized surface, formed of large (100) and (210) facets.

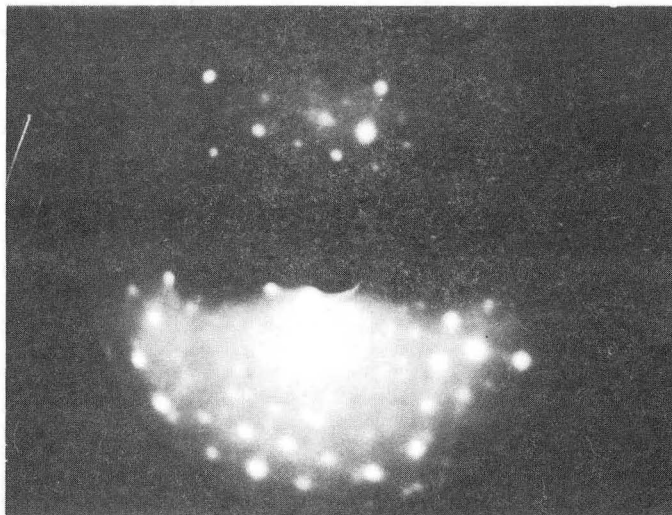




a)



b)



c)

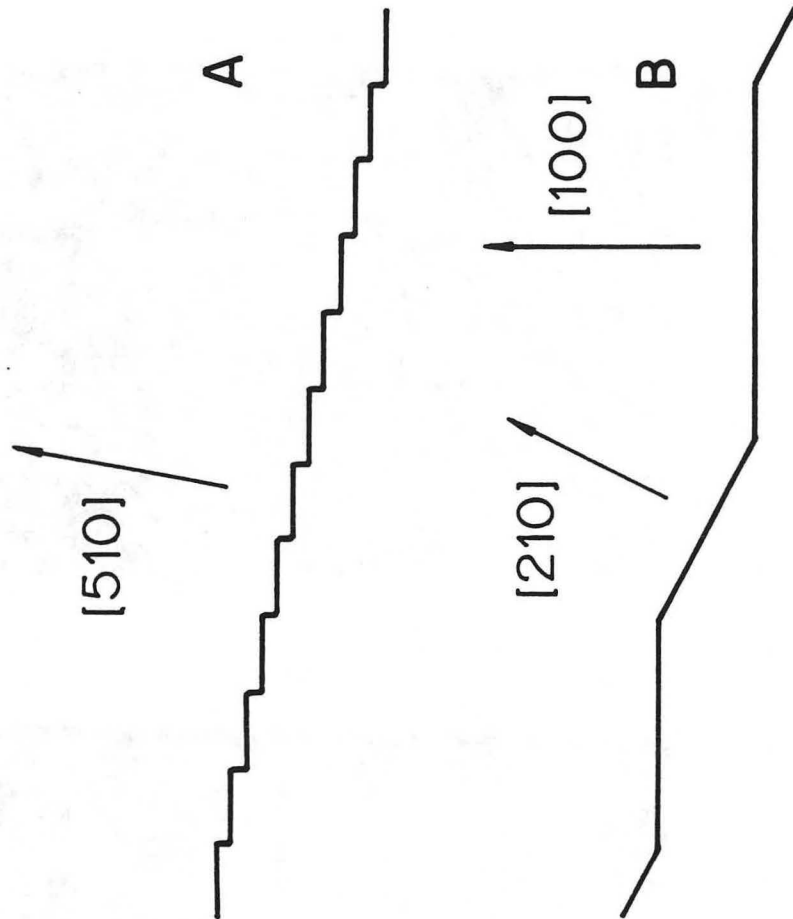


Figure 3.

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