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CHARACTERIZATION OF A TITANIUM PROMOTED SUPPORTED PLATINUM ELECTROCATALYST

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ABSTRACT

X-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), and extended x-ray adsorption fine structure (EXAFS), were used for the characterization of a highly dispersed Ti promoted Pt electrocatalyst. This bimetallic catalyst was prepared by addition of $TiCl_4$ to a methanol-water solution containing Pt on carbon black catalyst in suspension. Following filtration and air drying (300°C), heat treatments up to 1200°C under flowing argon were performed to promote the formation of Pt-Ti alloy phases. XPS indicated the development of a peak at 454.9 eV peak (assigned to Ti in Pt_3Ti), which increased in area with heat treatment temperature. Following the 1200°C heat treatment ~50% of the Ti was converted to the intermetallic phase, Pt_3Ti. The Pt(4f) photoelectron line shifted (+0.3 eV) to 71.2 eV following the 1200°C heat treatment, the Pt(4f) binding energy for bulk Pt_3Ti. XRD showed only fcc reflections, indicating the excess Ti present as TiO_2 was x-ray amorphous. Prior to heat treatment of the Ti impregnated catalyst, the fcc reflections indicated a lattice parameter of 3.927 Å, identical to that for pure Pt. As heat treatment temperature increased the lattice parameter decreased to 3.906 Å, the value for bulk Pt_3Ti. Particle size estimates indicated a progressive increase in the crystallite size of Pt alloy phase with temperature to a final size of ~150 Å at 1200°C. Definitive proof of an ordered Pt_3Ti phase was the presence of superlattice diffraction lines from materials heated above 900°C. EXAFS of these catalysts confirmed the conversion of an initial Pt-TiO_2 mixture to Pt_3Ti at 900-1200°C heat treatment temperatures.

INTRODUCTION

Platinum has the highest catalytic activity for oxygen reduction of any of the pure metals [1], and when supported on a conductive carbon black forms the standard electrocatalyst for phosphoric acid fuel cell air cathodes [2]. Modifications to the standard supported Pt catalyst have been attempted in recent years in an effort to develop higher performance cathodes. Recently, a series of patents have appeared [3] claiming enhanced activity for oxygen reduction for Pt catalyst promoted by impregnation with a variety of base-metal oxides, especially the Group IV and V transition metal oxides. In some instances, claims are made for improved catalysis resulting from the formation of alloy phases which formed during heat-treatment of the oxide impregnated catalyst. However, the claims for alloy formation are not accompanied by supporting evidence from characterization studies. Alloying of Pt with Group IV and V transition metals is described in the Engel-Brewer bond model [4] as giving rise to a sharing of Pt d-electrons with the unfilled d-orbitals of the base metal. Since most classical theories of metal catalysis ascribe the unique catalytic properties of the Pt-group metals to d-electrons, it is reasonable to anticipate that a change in the catalytic properties of Pt will occur upon alloying with Group IV metals, like Ti.

In this paper, we report the preparation and characterization of a carbon supported Pt catalyst impregnated with TiO_2 and heat-treated to successively higher temperature to promote alloy formation. The techniques employed are x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and extended x-ray absorption fine structure spectroscopy (EXAFS). In combination, these techniques show the progressive conversion of TiO_2 to Pt-Ti alloy phases at

progressively higher heat-treatment temperatures, resulting eventually in the formation of crystallites of the ordered (intermetallic) phase Pt_3Ti.

PREPARATION

All catalysts were prepared starting from a commercially available carbon supported Pt catalyst obtained from the Prototech Company (Newton Highlands, MA). The Pt loading of the material used was 10% by weight with a narrow particle size distribution of from 15-30 Å. High purity (3N) liquid pure $TiCl_4$ was the source of titanium, used as received from Alfa. A series of catalysts we designate as Series I was prepared by addition of a calibrated volume of $TiCl_4$ to an agitated 1:1 methanol:water solution containing the Pt catalyst in suspension. The volume of $TiCl_4$ added was sufficient to yield about 1.5 wt. % Ti in the final catalyst, or about twice the stoichiometric amount for complete conversion of all Pt to Pt_3Ti. For the Series II catalysts the pH of the solution was adjusted after addition of $TiCl_4$ to 10 by drop-wise addition of NH_4OH. The catalyst was brought to dryness in an ultrasonic mixer. Large chunks of catalyst were then ground with a mortar and pessel to obtain the fluffy, fine, as-prepared catalyst. Subsequent heat treatments were all run for 2 hours under flowing high purity He. The 700°C and 900°C heatings were done in a Pt boat, while the 1200°C heating was performed in a graphite boat.

The catalysts were subjected to stability testing in phosphoric acid at standard fuel cell operating conditions, 98% acid, 170°C, potentials of 0.6 to 0.9 V (RHE). The catalysts were fabricated into electrodes of the type described by Kunz and Gruver [5]. For the purposes of stability testing these electrodes were immersed in oxygen saturated electrolyte, and subjected to slow

(2 mV s^{-1}) potential cycling between 0.9 V and 0.6 V (versus reversible hydrogen electron in same electrolyte, RHE). After ca. 6 hrs., the electrodes were removed, extensively rinsed with distilled water, and dried in a vacuum dessicator. After drying, the catalysts were analyzed by x-ray fluorescence, XPS, and XRD in electrode form.

INSTRUMENTATION

X-ray photoelectron spectroscopy (XPS) was performed in a Physical Electronics 548 Auger/ESCA system. The spectrometer uses a Mg Ka (1253.6 eV) x-ray source and a double-pass cylindrical mirror analyzer. The system is ion pumped with a base pressure following bake out of 4 x 10^{-8} Pa. Specimens were introduced into the analysis chamber by a rapid introduction probe. Binding energies were referenced to 83.8 eV for the Au 4f 7/2 photoelectron peak. For analysis the catalyst specimens were mixed with Teflon powder (10 wt%) as a binder and then pressed into a 5mm hole drilled through a 2cm x 1cm x 1mm aluminum holder. The aluminum holder was then mounted onto the probe tip. The data collection and analysis system used for XPS have been described elsewhere [6].

X-ray diffraction (XRD) was performed using Cu Ka radiation in a Siemens D-500 diffractometer. Powder specimens were held in a 2.5cm x 2.5cm x 1mm trough cut into the surface of a lucite block. Powders were pressed into the trough with a glass slide to obtain an even, smooth distribution of the powder.

X-ray fluorescence (XRF) spectra were collected with a Tracor X-ray Spectrace 4020. An Itel 8086 microprocessor controls data acquisition and analysis. A Rhodium x-ray source and a Si(Li) detector are used for excitation

and collection of the fluorescence data.

Extended x-ray absorption fine (EXAFS) structure experiments were performed on the new beamline VI at SSRL. The experiments were performed with beam conditions of 3 GeV and 60 ma. The powders were mounted on a porous graphite substrate again using Teflon as a binder. The EXAFS specimen holder and fluorescence detector was obtained from F.W. Lytle [7]. Fluorescence detection was chosen owing to the superior S/N capability in highly dispersed systems [8]. Data evaluation was performed using software provided by Sandstrom [9]

RESULTS

A. Characterization Results of the Series I Pt-Ti Catalysts

A.1 XPS Analysis

X-ray photoelectron Spectroscopy was employed to identify the chemical state of the Ti along the preparation pathway. Titanium (2p), platinum (4f), carbon (1s), and oxygen (1s) photoelectron spectra were collected from each specimen. Survey scans were also collected to observe the presence of any contaminants. Bulk polycrystalline Pt_3Ti was analyzed to obtain standard Ti(2p) and Pt(4f) binding energies for the alloyed state, while the Ti(2p) and Pt(4f) binding energies for TiO_2 and metallic Pt were obtained from oxidized Ti foil and Pt foil, respectively. Binding energies of TiC, TiO and $TiCl_3$ were obtained by analysis of these powders mixed with graphite. A summary of the binding energies for these standard compounds is given in Table 1.

Titanium spectra from Series I catalysts are shown in Fig. 1. With increasing temperature the peak characteristic of intermetallic Ti (ca. 455 eV)

grew dramatically. Titanium to platinum atomic ratios calculated from fitted XPS spectra quantitatively represent the changing form of the titanium (Table 2). As temperature increased the intermetallic Ti to Pt ratio rose to a level equal to that of the TiO_2 to Pt, as expected, since twice the stoichiometric amount of Ti for formation of Pt_3Ti was used in the preparation. A more surprising observation is the apparent "loss" of Ti on going from the as-prepared to the 700°C specimen. We know from the elemental analysis that Ti is not lost in heat-treatment. The apparent "loss" indicated by XPS data can be explained in terms of the relative escape depths of the Ti and Pt photoelectrons, making certain assumptions about the distribution of TiO_2 in the catalyst matrix following impregnation. The Ti(2p) photoelectrons have lower kinetic energy, and thus shallower escape depth, than the Pt(4f) photoelectrons. If it is assumed that impregnated TiO_2 is deposited preferentially on the "exterior" of carbon aggregates (containing Pt uniformly dispersed), then the apparent "loss" can be rationalized in terms of Ti diffusion into the "interior" of carbon aggregates and resultant attenuation of Ti(2p) photoemission (relative to the uniformly distributed Pt). In this context, "interior" and "exterior" refer to geometries relative to electron energy analysis, i.e. as "seen" by the spectrometer.

The platinum spectra had small but reproducibly observable changes in response to the heat treatments. In all cases, deconvolution of the Pt(4f) spectra indicated the presence of a minor Pt state with a binding energy of ~2.5 eV higher than the metallic peaks as indicated by Fig. 2. While we have not assigned this state to a specific Pt compound, it is clear that this state is not related to the formation of the intermetallic phase. The Pt(4f, 7/2) binding energies for all the Series I samples are summarized in Table 3. The

changes in binding energy may be interpreted in the following manner. Initially the Pt is in a mixed valence state with chemisorbed oxygen or possibly a surface oxide giving rise to the high binding energy component [10]. After 700°C heat treatment, the adsorbed oxygen is removed and/or the oxide is reduced, leaving the Pt mostly as metal. Upon further heating to 900 and 1200 degrees, significant alloying occurs causing the shift of the Pt(4f, 7/2) binding energy to a value indicative of Pt in Pt_3Ti.

Observed impurities were sulfur, chlorine, and oxygen. Sulfur and oxygen have been found to be impurities in the carbon support. Chlorine, due to the $TiCl_4$ starting material, is a significant impurity in the as-prepared specimen, e.g. 3.2 at %. Upon heating to 700°C, most of the chlorine is lost leaving only 0.5 at %. Catalyst composition (in at %) determined by XPS is listed below for the as-prepared catalyst:

C	-	88.67%	O	-	5.85%
Cl	-	3.20%	S	-	0.75%
Pt	-	0.92%	Ti	-	0.58%

X-ray fluorescence (XRF) analysis was performed to obtain an indication of the total elemental Pt/Ti ratio. The results are summarized in Table 3. Prior to heat treatment the observed Pt to Ti ratio was approximately one-half that of a standard Pt_3Ti. This was as expected considering the two-fold excess Ti present in the catalyst preparation. Upon heat treatment to 1200°C the ratio dropped to approximately one-fourth that of bulk Pt_3Ti. The drop in the Pt/Ti ratio might be due to attenuation of the low energy x-rays by the larger particles. However, in such a case the lower energy Ti(Ka) photons would be attenuated to a greater extent causing an increase in the ratio. The most

likely cause is platinum volatilization as a chloride or oxide. A sufficient amount of oxygen and chlorine are present, and many of the possible Pt compounds are volatile at temperatures above 600°C.

A.2 XRD Analysis

X-ray diffraction is a powerful technique for the determination of crystalline structure and particle size estimates of dispersed systems. The ordered alloy Pt_3Ti has an fcc structure (Ll_2, Cu_3Au type) with a_o = 3.906.

We know from the XPS data that a significant fraction of the Ti persists as TiO_2. Figure 3a shows the diffraction pattern from the as-prepared specimen, very broad Pt and graphite reflections are observed. The absence of TiO_2 reflections in any of the diffraction patterns indicates that the TiO_2 must be amorphous.

X-ray diffraction studies of the Series I catalysts are sumarized by Table 4. Lattice parameter values diminish steadily from the as-prepared 3.926 Å, to the 1200°C heat treated specimen 3.906 Å. Particle size calculated from the linewidths of the (111) reflections indicate a rapid jump from 48 Å to 110 Å upon heating to 700°C, then more slowly to 140 Å after 1200°C heat treatment. For both the 900 and 1200°C heat treated catalysts, superlattice lines were observed, indicative of the formation of the ordered alloy phase. The relative intensity of superlattice lines is indicated by the scan shown in Fig. 3b. Calculation of the order parameter [11] indicated the 900°C catalyst to be 67% ordered, assuming the 1200°C catalyst was fully ordered.

A.3 EXAFS Analysis

Titanium K-edge EXAFS data were analyzed to follow changes in the nearest neighbor configuration around Ti atoms during heat treatment. Because EXAFS is caused by electron backscattering, the spectra are very sensitive to changes in coordination as dramatic as would occur in the transition from an oxide to an alloy due to the large differences in scattering cross-section between O^{2-} and Pt (or even between Ti and Pt). For the characterization of supported catalyst, EXAFS has an important advantage over XPS for chemical state determination in that it is a bulk technique, i.e. there is no screening of fluorescence from Ti "buried" in the carbon support, as is the case for photoemision. In analyzing the EXAFS data, we used a combination of the "fingerprint" method with $\chi(k)$, and quantitative analysis using the radial structure functions derived from the Fourier transform of $k^3 \chi(k)$. The $\chi(k)$ spectra of the Series I catalysts are compared directly to those for the standard compounds TiO_2, TiC and Ti metal as shown in Fig. 4. The spectrum for the 1200°C heat-treated catalyst is virtually identical to that from a Pt_3Ti crystal, and the spectrum for the catalyst prior to heat-treatment is virtually identical to that for TiO_2. After 700 and 900°C heat-treatment, there are features that are common to both the TiO_2 and Pt_3Ti state. TiC has oscillatory features very similar to those for Pt_3Ti, which is expected since the Ti-Ti bond distances (second coordination shells) are close to those for Ti-Pt in Pt_3Ti. Fourier transform analysis of the $\chi(k)$ data for TiC indicated that scattering from the C atoms was not resolvable, i.e. the $\chi(k)$ is made up entirely of scattering from the Ti containing coordination shells. However, the <u>amplitudes</u> of the oscillations are four times larger in Pt_3Ti than in TiC,

due to the higher scattering cross-section of Pt. The feature at $k \simeq 5$ and the three relatively strong oscillations for $9 < k < 12$ (relatively weak in TiC) are characteristic of the Pt coordination about Ti, and these features are clearly evident in the 900°C sample, and even discernable in the 700°C sample. In the 1200° sample, there appears to be no contribution from the TiO_2 that must be left over (and observed to be present by XPS). As was the case for scattering from C atoms in TiC, scattering from oxygen nearest neighbors has a much lower amplitude contribution than scattering from Pt nearest neighbors, and the TiO_2 signal is lost in comparison to the signal from those Ti atoms that have formed the Pt_3Ti phase.

B. Characterization of the Series II Pt-Ti Catalysts

B.1 XPS Analysis

The Ti(2p) XPS results obtained from the Series II catalyst were disappointing in that despite an identical amount of Ti present as the Series I catalysts, photoelectron signals were much weaker. Meaningful spectra could only be obtained after long counting times. Smoothing of these poor quality spectra was required to perform even crude data analysis. The as-prepared catalyst had Ti present as TiO_2 while on the 900°C and 1200°C catalyst the only Ti peak observable was at ~455 eV, suggesting alloy formation. Unlike the Series I catalyst there was no TiO_2 peak appearing along with the intermetallic peak on the 900°C and 1200°C specimens, and no Ti 2p photoemission could be obtained from the 700°C specimen (!).

The same impurities were observed on the Series II samples as with Series I:

oxygen and sulfur from the support, and chlorine remaining from the titanium addition procedure. XRF of the as-prepared and 1200°C catalysts indicate a lowering in the Pt/Ti metal ratio following heating. Similar to the Series I catalyst results, the as-prepared specimen has a Pt/Ti ratio about a factor of two less than that for bulk Pt_3Ti. The 1200°C catalyst Pt/Ti ratio is even lower, again apparently from platinum loss due to either volatilization as an oxide or chloride.

X-ray diffraction results are summarized in Table 5. Lattice parameter values show that only at 1200°C did sufficient alloying occur to form the Pt_3Ti phase. Superlattice lines confirm the formation of Pt_3Ti following the 1200°C heat treatment. Intermetallic formation coincided with significant particle aggregation, i.e. a four-fold increase in particle size was observed between the 900 and 1200°C heat treatment. The absence of superlattice lines and the high lattice parameter value indicate that 900°C heat treatment did not promote significant alloying. This result for the 900°C catalyst, however, is in disagreement with our XPS observation of the presence of some alloy phase. XPS, however, probes only a small depth into the catalyst, and it is possible that some alloy phase has formed on the "exterior" surface while insufficient bulk properties were present to be observed by XRD. The lattice parameter value for the as-prepared specimen is listed as an aproximate value because of the extreme broadness of the peaks. The (111) reflection was used for the lattice parameter calculation, but a reflection at a greater backscattered direction is more favorable for lattice parameter calculation. The (311) reflection, typically used for this determination, was too weak to obtain a useful result.

Titanium K-edge EXAFS results indicated that as-prepared, 700 and 900°C heated specimens all had first neighbor coordination close to TiO_2. This

result is as expected from the XRD data, although it is again contrary to the XPS Ti(2p) data from the 900°C catalyst. Again, this must be due to the limited sampling depth of XPS. The 1200°C result showed the four strong features which correlate to the expected coordination shell distances of Ti and Pt in Pt_3Ti.

C. Stability of the Catalysts in Phosphoric Acid

TiO_2 powder was observed to dissolve, slowly, in hot, air saturated, phosphoric acid. It was expected, therefore that elemental analysis of the catalysts would show Ti loss, since there is at least a 50% excess of Ti as TiO_2. X-ray fluorescence analysis (Table 3) did show a significant loss of Ti after stability testing, but the loss was much smaller for the 1200°C heat-treated catalyst, indicating some stabilization of Ti by alloying. This was confirmed, in the case of Series I catalyst, by XPS and XRD analysis. The Ti(2p) spectra for the 1200°C catalyst indicated that after stability testing the 2p line at ~458 eV had essentially disappeared, leaving only a strong peak at ~455 eV characteristic of the alloy. The XRD results from the Series I catalysts after stability testing are summarized in Table 6. The testing produced effects on all three XRD parameters, the lattice parameter of the fcc phase(s), the line widths and the appearance of superlattice lines. All the (111) line profiles were wider after testing, and in the 700 and 900°C catalysts the lattice parameters changed towards that for pure Pt. In the 900°C catalyst, the superlattice lines were nearly extinguished. There are two interpretations of the line broadening observed after stability testing: i.) the particle size of fcc phase(s) decreased; ii.) there was preferential

dissolution of Ti from the smaller alloy crystallites, leaving Ti in only the largest (20-40 nm) crystallites. We suggest the latter is the more plausible. The separation in 2Θ between the (111) reflections for Pt and Pt_3Ti is only 0.2^o (for Cu-K_α), which is too small to resolve if the particle size of both phases is less than ca. 40 nm, as is the case here. Further, analysis of tested catalyst by transmission electron microscopy failed to detect any significant change in crystallite size of the 900 and 1200°C catalyst due to testing. It appears from the stability study that Pt_3Ti alloy crystallites are stable in phosphoric acid at fuel cell air cathode conditions, provided the alloy crystallites are sufficiently large, e.g. typically larger than 20 nm. However, smaller alloy crystallites appear unstable, with phase separation caused by Ti dissolution. It may also be that the surface of the large alloy crystallites is devoid of Ti, a result indicated by surface analysis of Pt_3Ti alloy crystals in our laboratory.

DISCUSSION

At the start of this study, we did not anticipate that the method of titanium impregnation would have as dramatic an effect on the chemistry occurring during heat-treatment as it seems to have from these results. The patent by Jalan and Landsman [3] claims that a supported Pt-Ti alloy can be prepared by impregnating the Pt on carbon catalyst with high surface area TiO_2 by physical blending followed by heat-treatment to 900°C. In our study, we found that physical blending of TiO_2 and the method we termed here as the Series II resulted in identical material, as far as our characterization was concerned. When $TiCl_4$ is added to an alkaline solution, as was done in the

Series II preparation, rapid hydrolysis occurs to form a cloudy suspension, most probably a $TiO_2 \cdot xH_2O$ colloid [12]. It is not surprising, then, that the physical blending of TiO_2 and the Series II resulted in the same material, since the Series II preparation results in the formation of TiO_2 (hydrate) in a physical mixture with the Pt on carbon catalyst suspended in the solution. As our characterization study has shown, there was no evidence of any alloy phase formation at a heat-treatment temperature of 900°C or lower for the Series II catalysts (or for catalyst made by physically blending TiO_2). We attribute this to non-uniform distribution of the titanium in the Pt/carbon matrix, which made it impossible for the Pt and Ti phases to be in physical contact in order to react and form the alloy phase. At the very high temperature of 1200°C, we know from hot-stage electron microscopy [13] that at this temperature Pt atom diffusion occurs resulting in particle size growth via Ostwald ripening. At this condition, alloy phase formation can occur even when the TiO_2 and Pt particles are widely separated in the matrix due to the Pt atom mobility, and, in fact, this was the only condition from which we did observe alloy formation in the Series II preparation (after 1200°C).

It is possible to rationalize the XPS results, or non-results in this case, for the Series II catalysts on the basis of non-uniform distribution of the titanium in the Pt/carbon matrix. To the spectrometer, the titanium appeared to be "buried" in the carbon. The carbon prime particle size in Vulcan XC-72 is ca. 30 nm, and the mean agglomerate (collection of fused prime particles) size is ca. 300 nm. Physical blending of TiO_2 with the carbon black cannot produce a scale of interphase contact finer than the carbon agglomerate size, so that one might expect that at best each TiO_2 particle is surrounded by at least "one-layer" of carbon aggregate. Since the mean escape depth for Ti

photoelectrons (with an Mg anode) is less than 100 nm, the spectrometer does not "see" the TiO_2 phase.

On the other hand, with the Series I preparation we were able to collect reasonably high quality XPS data, and alloy formation was evident even at the low heat-treatment temperature of 700°C. We attribute this very different state of titanium in these catalysts to the different chemistry occurring when hydrolysis of $TiCl_4$ occurs at low pH. When $TiCl_4$ is added to water in the absence of a pH buffer, or to a solution slightly acidified with HCl, hydrolysis results in the formation of the sparingly soluble titanyl ion and a lowering of the pH [12]. In the Series I preparation, the relative volumes of reactants were such that the pH was lowered from ca. 6.5 to 2 upon addition of $TiCl_4$; at this pH titanyl ion has moderate solubility (e.g. 0.1 mM). There is some indication from the increase in Pt crystallite size following the titanium impregnation (no heat-treatment) that some fraction of the Pt may be dissolved in this acid chloride solution. During evaporation to dryness, the titanium is either adsorbed onto the carbon as a titanyl complex, or precipitates as some kind of oxychloride phase into the carbon matrix, or both. During this stage, any Pt dissolved would be redeposited onto the carbon, and possibly incorporated into the titanium phase/complex at this time. Because impregnation proceeds via a soluble species, it is more likely to result in distribution of the titanium within the Pt/carbon matrix on a finer scale than impregnation via an insoluble oxide phase, as in the Series II method. The XPS results clearly indicate that a more uniform distribution of titanium in the Pt/carbon matrix occurred in the Series I preparation. Reasonable (according to their relative sensitivities and atomic concentration) Ti(2p) to Pt(4f) intensity ratios were observed, indicating that titanium phases were

distributed "on-top-of-carbon" in some fashion similar to the distribution of the Pt crystallites. Both XRD and EXAFS indicated a progressive increase in the conversion of titanium into the alloyed state with increasing temperature. In previous surface studies of the Pt-Ti system [14] in this laboratory, we had observed a similar relation in the reduction of TiO_2 overlayers on Pt to form the ordered alloy. Thus, the Series I supported Pt-Ti catalyst appear to behave, from the reaction between phases, in the manner expected for Pt and titanium phases in physical contact.

It is interesting to note the absence of TiC as an intermediate phase forming in reduction of the TiO_2. While this reaction might be expected intuitively, in fact the reduction of TiO_2 by carbon in an inert atmosphere is not very favorable from a thermodynamic standpoint. Using the JANAF Thermochemical Tables, one finds that considering the equilibria

$$TiO_2 + 2C \rightleftharpoons TiC + CO_2$$

$$TiC + O_2 \rightleftharpoons TiO_2$$

the equilibrium partial pressures of oxygen and/or CO_2 are impractically low, considering that the carbon black we are using contains ca. 5 at % oxygen, and the inert gas at least a few ppm oxygen. If the equilibria are changed to reflect the formation of Pt_3Ti as the reduced state instead of TiC, the equilibrium pressures for oxygen and/or CO_2 become more realizeable, since the free energy of formation of Pt_3Ti is ca. 100 kJ/mol more negative than for TiC [15]. In practice, the actual reducing reactions are not known, but considering that the carbon black contains significant levels of hydrogen and

oxygen, and the inert gas contains some level of oxygen, the most probable reactions are:

$$TiO_2 + 2\ H_2 + 3\ Pt \rightleftharpoons Pt_3Ti + 2\ H_2\ O$$

$$TiO_2 + 2\ CO + 3\ Pt \rightleftharpoons Pt_3Ti + 2\ CO_2$$

where the equilibrium favors the formation of intermetallic if $CO/CO_2 > 10^2$ and/or $H_2/H_2O > 10^3$ (at 1000^oC).

The results from the stability testing of the Pt-Ti catalysts indicate that even in alloy form the titanium adatoms may not be stabilized towards dissolution. Because these catalysts all had an excess amount of titanium, and therefore some unalloyed titanium was always present, it was difficult to determine by elemental analysis of tested catalyst whether the alloyed titanium was lost as well. However, the XRD analysis of tested catalyst clearly indicated a significant weakening of the superlattice lines for the ordered alloy phase after stability testing, an indication that even the alloyed titanium is not stable at phosphoric acid fuel cell cathode conditions. The same indication was also obtained from surface analysis of Pt_3Ti crystals subject to comparable stability tests as performed here. It is surprising, therefore, to find that these catalysts do have improved activity in phosphoric acid fuel cell cathodes relative to the parent Pt on carbon catalyst from which they were derived. This improved activity claimed in the patents for Pt-base metal "alloy" catalysts has been confirmed in studies in our laboratory [16] using catalysts prepared according to procedures described in the patents. The reason(s) for this enhanced activity remain unclear, but it seems certain that

it is not related to new properties of a surface containing titanium in coordination with platinum, since Pt-Ti alloy surfaces do not contain Ti after exposure to fuel cell cathode conditions.

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Table 1. Binding Energies for Pt and Ti in Standard Compounds and Chemical Shifts.

	Pt(4f, 7/2)	Ti(2p, 3/2)	Δ B.E.
Pt foil	70.9		ref.
Pt_3Ti	71.2		+0.3
Ti foil		453.8	ref.
TiO		454.6	+0.8
TiC		454.7	+0.9
$TiPt_3$		455.1	+1.3
TiO_2		458.5	+4.7
$TiCl_3$		459.4	+5.6

Table 2. Integrated XPS Intensity Ratios of Ti(2p, 3/2) to Pt(4f, 7/2). Signals for Heat-Treated Catalysts.

Chemical State of Ti	As Prepared	700°C	900°C	1200°C
As TiO_2	1.89	0.49	0.48	0.47
As "alloy"	0	0.09	0.22	0.55
Total Ti	1.89	0.58	0.70	1.02

Table 3. Relative Intensities of Pt and Ti X-ray Emission Signals from Catalysts before and after Stability Testing.

Catalyst	Untested Pt/Ti Ratio	Tested Pt/Ti Ratio
Series I As-Prepared	42:1	57:1
Series I 1200°C	29:1	48:1
Series II As-Prepared	50:1	88:1
Series II 1200°C	40:1	57:1
Pt_3Ti Standard	110:1	--

Table 4. XRD Analysis of Series I Catalysts.

Catalyst	Lattice Parameter	Particle Size	Super-lattice
As-Prepared	3.926 Å	48 Å	No
700°C	3.916 Å	110 Å	No
900°C	3.907 Å	125 Å	Yes
1200°C	3.906 Å	144 Å	Yes

Table 5. XRD Analysis of Series II Catalysts.

Catalyst	Lattice Parameter	Particle Size	Super-lattice
As-Prepared	3.927 Å	<40 Å	No
700°C	3.922 Å	50 Å	No
900°C	3.922 Å	70 Å	No
1200°C	3.908 Å	280 Å	Yes

Table 6. XRD Analysis of Series I Catalysts After Stability Testing in Phosphoric Acid.

Specimen	Parameter	(111) Line Widths (°2Θ) Before	After	Superlattice
As-Prepared	3.927 Å	2.2	2.16	No
700°C	3.928 Å	1.0	.90	No
900°C	3.910 Å	.90	.82	Very Weak
1200°C	3.907 Å	.80	.76	Yes

FIGURE CAPTIONS

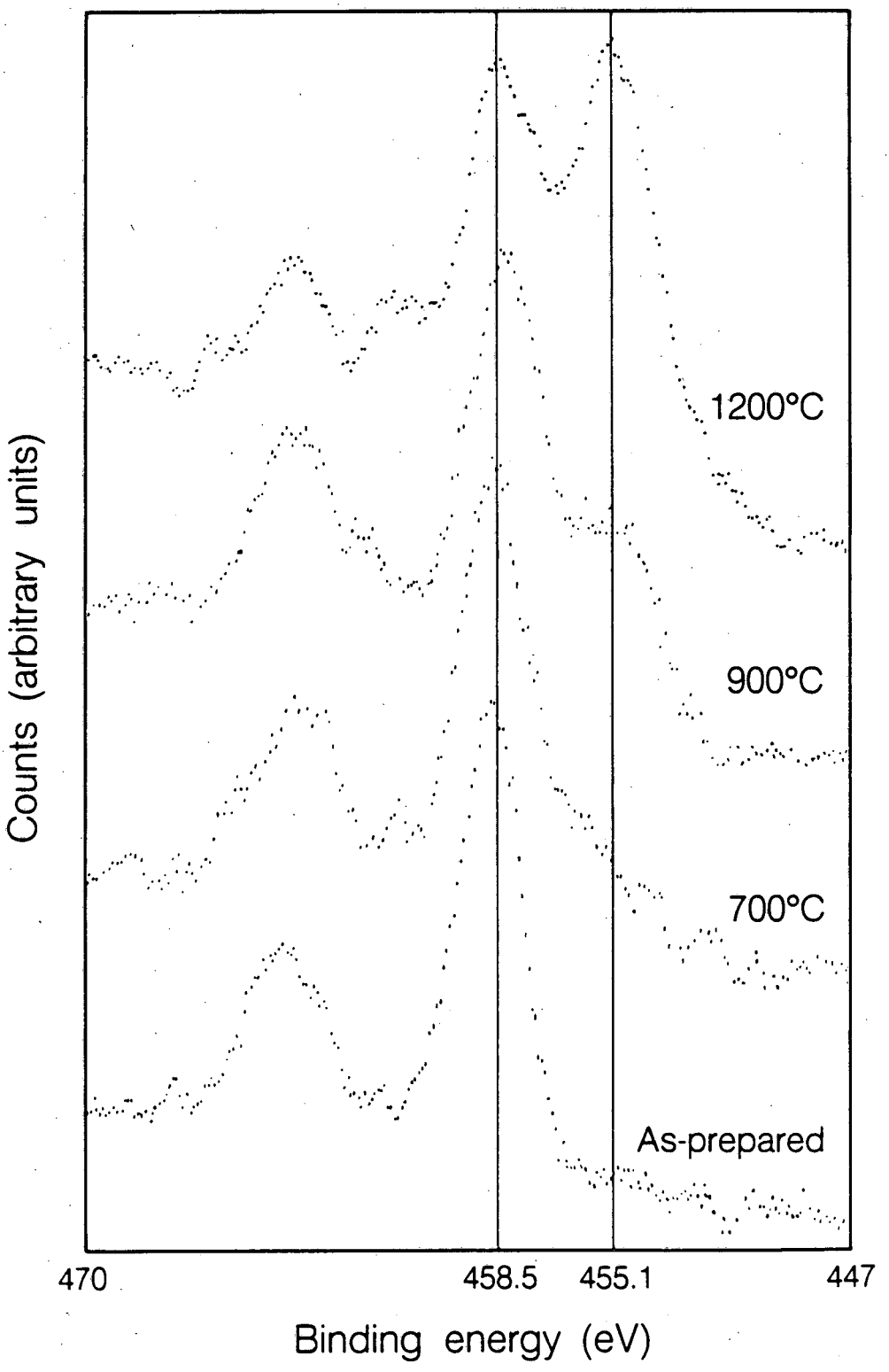
Fig. 1. XPS spectra from Ti(2p) region for Series I catalysts as a function of heat-treatment temperature.

Fig. 2. XPS spectra from Pt(4f) region of standard Pt on carbon catalyst after air exposure.

Fig. 3a. X-ray diffraction scan of the TiO_2 impregnated standard Pt on carbon catalyst in the as-prepared state;

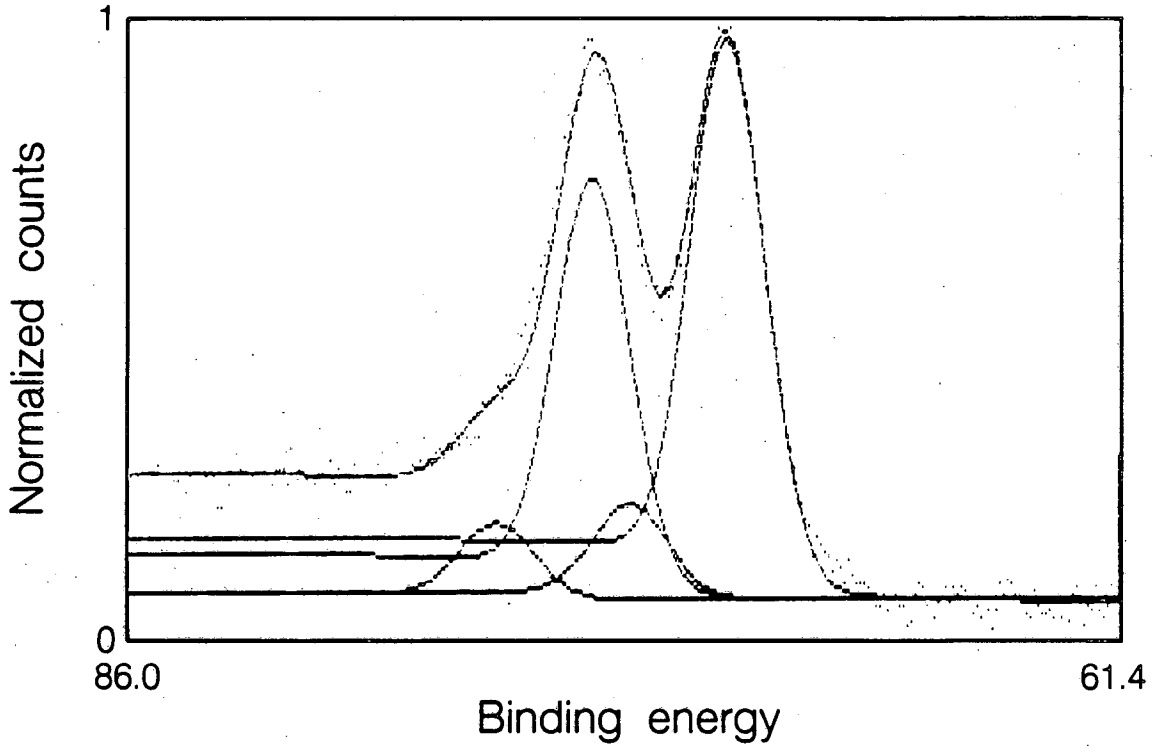
3b. Scan for the 1200°C heat-treated catalyst. Graphite (002) and (10) reflections are at ca. 25 and 43° respectively. Superlattice lines are indicated. Cu-K_{α} radiation.

Fig. 4. Normalized EXAFS spectra for the standard compounds Ti (foil), TiC, TiO_2, and the Series I catalysts. Dashed lines denote features unique to the standard spectrum for Pt_3Ti.



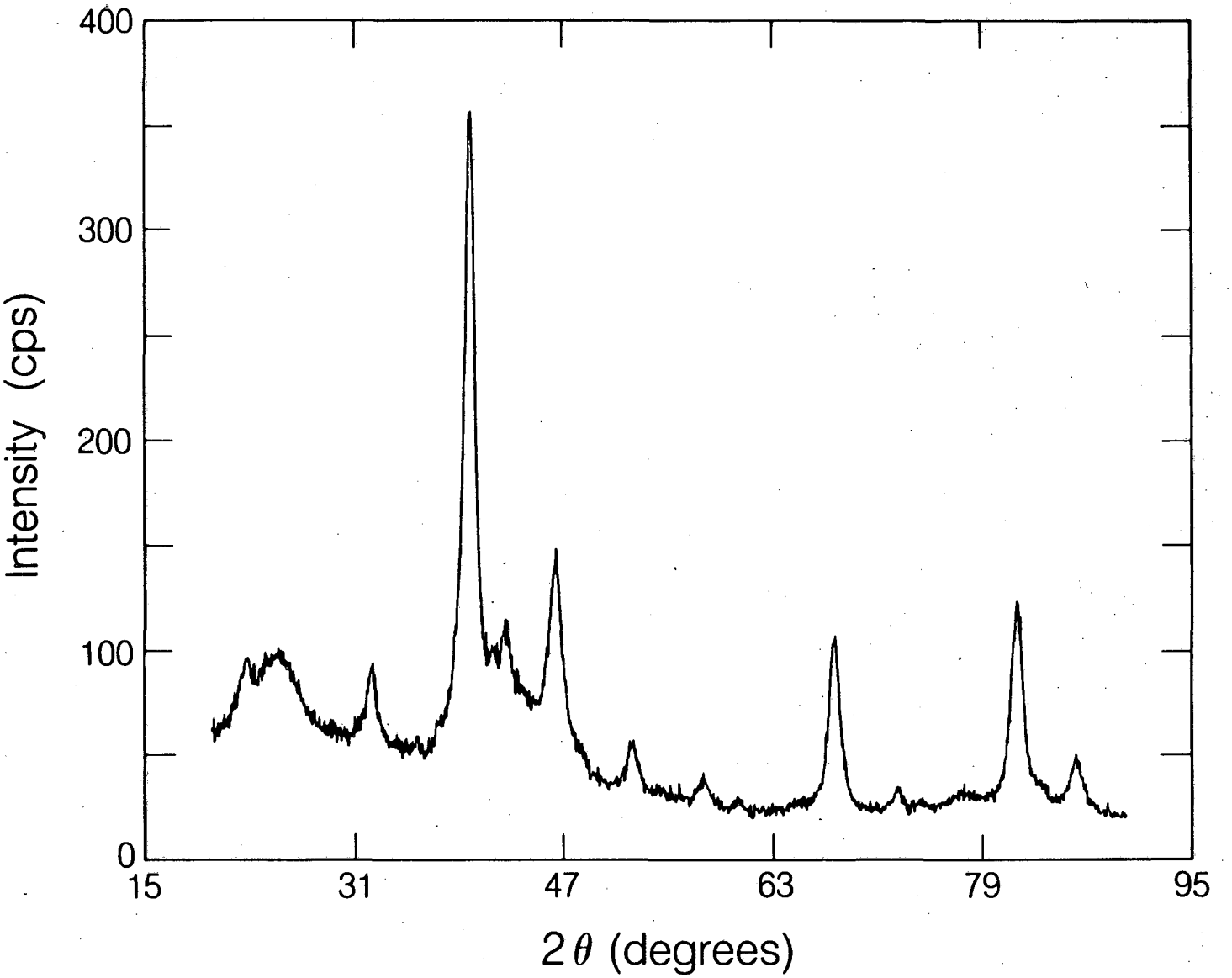
XBL 855-8896

Fig. 1



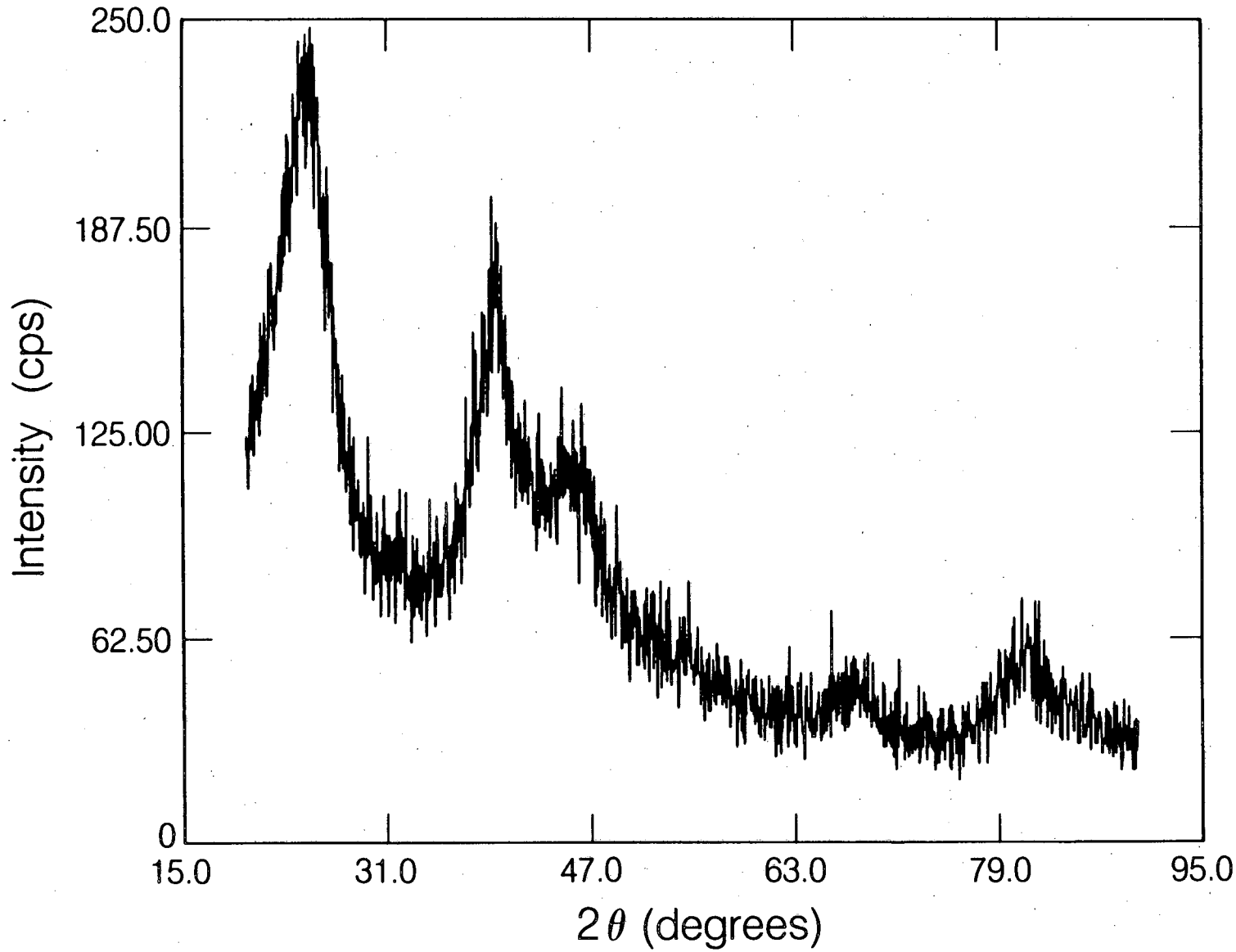
XBL 855-8897

Fig. 2



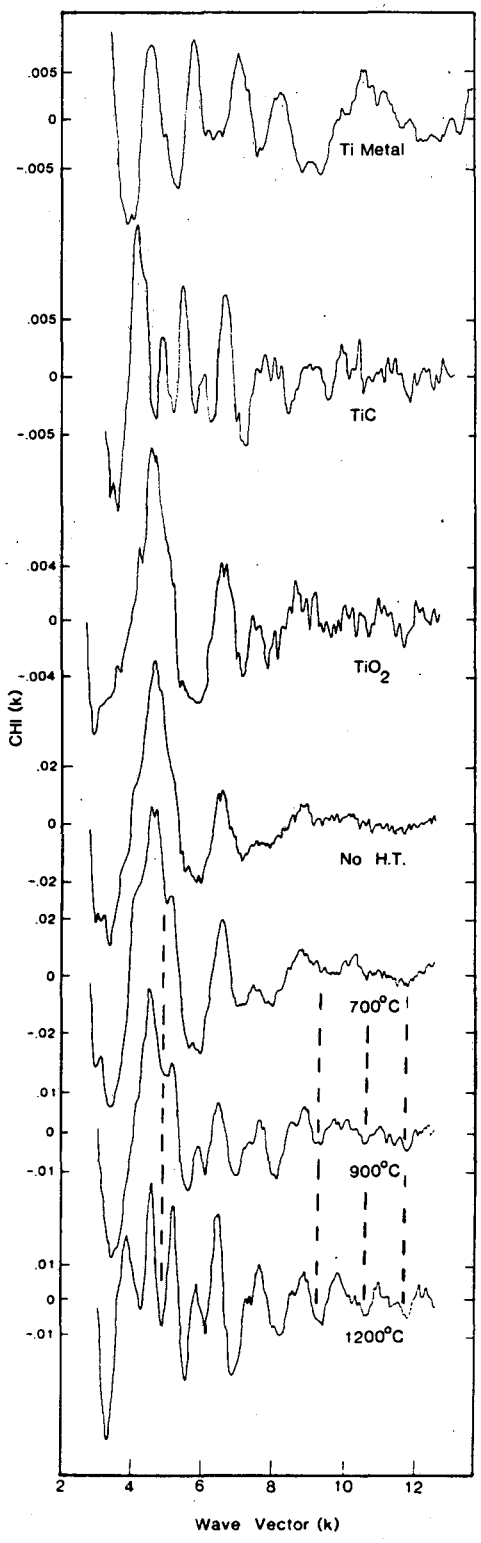
XBL 855-8895

Fig. 3a



XBL 855-8894

Fig. 3b



XBL 857-3020

Fig. 4

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