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INVESTIGATION OF MECHANISMS FOR ELECTROCHEMICAL CATALYSIS

THIRD QUARTERLY REPORT

By

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MAY 1967

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INVESTIGATION OF MECHANISMS FOR ELECTROCHEMICAL CATALYSIS

Quarterly Report
November 1, 1966 to January 31, 1967
Report No. 3

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FOREWORD

This report was produced in accordance with U. S. Army Contract No. DA-28-043-AMC-02205(E) by the Pratt & Whitney Aircraft Division of the United Aircraft Corporation. It discusses the work performed during the period from November 1, 1966, through January 31, 1967.

ABSTRACT

A program is being conducted to investigate the mechanisms of electrocatalysis with respect to the anodic oxidation of selected fuels by novel electrocatalysts in acid electrolyte at temperatures below 150°C and at ambient pressure. Major emphasis has been given to the investigation of the properties of transition metal silicides when surface-doped with platinum, gold, or both.

Conflicts had occurred in the data for silicides incorporated on gold and gold-plated current collectors, but investigation during the current quarter indicates that the conflicts resulted from platinum contamination. The study also showed that $TiSi_2$ exhibits some activity for hydrogen and methanol oxidation.

The electrochemical behavior of WSi_2 in acid electrolyte was studied and was found to be similar to that of $MoSi_2$. Both of these materials have tetragonal structures. VSi_2 and $TaSi_2$ also have similar electrochemical characteristics, and both have hexagonal structures.

Experiments with platinum-doped $TiSi_2$ electrodes indicates that relatively large amounts of platinum are required to obtain a catalytic activity which approaches that of an equivalent platinum sheet and that the utilization of the platinum is low. However, gold-platinum co-deposits on $TiSi_2$ exhibit markedly different behavior. The current obtained from the co-deposits as the ratio of gold to platinum was varied shows maxima at 50 and 70 weight percent of gold and a sharp minimum at 55 weight percent of gold. The maxima are higher than the levels of activity obtained with platinum alone.

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I. INTRODUCTION

A program is being conducted to investigate the mechanism of electrocatalysis with respect to the anodic oxidation of selected fuels by novel electrocatalysts in acid electrolyte at temperatures below 150°C and at ambient pressure. The studies are particularly concerned with the influence of surface properties on catalytic activity. The study is being conducted in an effort to identify active, low-cost catalysts for direct-energy conversion devices such as fuel cells.

The work performed during this report period involved study of the electrochemical behavior of selected transition-metal silicides and the effect on this behavior of adding trace amounts of gold and platinum to the surfaces of the silicides.

II. PROGRESS

A. CATALYTIC ACTIVITY OF $TiSi_2$

During the first quarterly period, $TiSi_2$ was found to have some catalytic activity when it was incorporated on a gold-plated platinum-sheet current collector. However, when a pure gold-sheet current collector was used, no activity could be detected. In both cases, a gold counter electrode was used. The understanding of this behavior was further complicated by data obtained prior to the current contract which indicated that certain silicides have considerable activity for hydrogen and methanol oxidation, whereas activity of the magnitude indicated by this data has not been duplicated during the current studies. Since the previous tests were performed with a platinum counter electrode, it was suspected that the high activity sometimes observed was caused by platinum contamination. Testing during this report period was directed toward verifying this hypothesis.

Testing was conducted in the original cell shown in Figure 1 of the first quarterly report. A pure gold sheet was used for the counter electrode and three different materials were used for current collectors, namely, platinum, gold-plated platinum, and gold. The electrolyte used was 1-molar H_2SO_4 at 50°C, with hydrogen and methanol as fuels. For each test point, the potential was maintained constant for ten minutes before current readings were taken to provide essentially steady-state data.

Initially, the activity of the current collectors was measured to obtain baseline data. Subsequently, the $TiSi_2$, mixed with 15 weight percent Teflon powder for binding, was pressed onto the current collectors and sintered at 250°C for five minutes. The current for hydrogen oxidation at a potential of 200 mv was then measured, and the results are shown in Table I.

TABLE I

Activity of $TiSi_2$ for Hydrogen Oxidation on Various Current Collectors

Current-Collector Material	Current for Hydrogen Oxidation at 200 mv (ma)	
	Current Collector Only	$TiSi_2$ on Current Collector
Platinum	1.2	0.3
Gold-Plated Platinum	0.3	0.2
Gold	0.05	0.12

Note: Corrosion current for $TiSi_2$ (nitrogen gas) at 200 mv was 0.005 ma.

As shown, the $TiSi_2$ on the platinum and the gold-plated platinum current collectors actually inhibited rather than increased the catalytic activity. On the gold current collector, however, the $TiSi_2$ increased the current over that of the gold current collector alone. Hence, it appears that $TiSi_2$ powder does have some activity for hydrogen oxidation. The higher currents obtained with the other electrodes are probably a combination of the current from the $TiSi_2$ and from the exposed platinum.

These results were then related to the tests performed prior to the current contract by testing the gold current collector with a platinum counter electrode. Further, to conform to the procedure used in the previous tests, a corrosion test using a nitrogen-saturated electrolyte was conducted before the oxidation tests were conducted. This was done to determine if the procedure allowed platinum to dissolve from the counter electrode and then diffuse over to and plate onto the working electrode. As for the previous tests, each potential was maintained for ten minutes before current readings were recorded. The electrolyte concentration and temperature were the same as used previously. The results obtained for the current collector alone and for the current collector with $TiSi_2$ powder are shown in Figure 1. These results show beyond any doubt that the gold sheet was contaminated with platinum from the platinum counter electrode, since considerable current was obtained with the current collector alone, and pure gold has no activity for hydrogen oxidation. The higher limiting current obtained with the $TiSi_2$ powder is attributed to the larger surface area produced by the powder. The limiting current obtained is approximately the same as that obtained prior to the contract for $TiSi_2$.

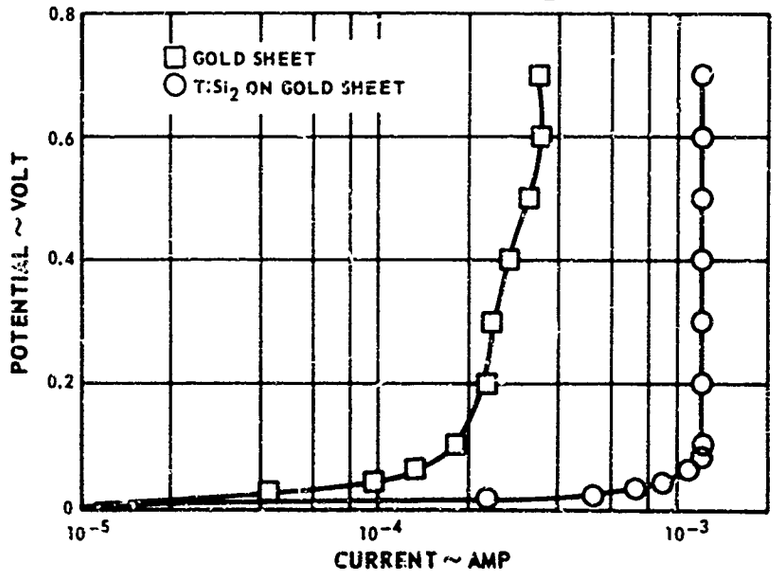

Figure 1 Activity of Gold Current Collector With and Without $TiSi_2$ Powder for Hydrogen Oxidation When a Platinum Counter Electrode is Employed

Additional tests were performed for a gold-sheet working electrode and for $TiSi_2$ supported on the gold sheet in the cell shown in Figure 1 of the second quarterly report. A gold counter electrode was used for these tests to avoid platinum contamination. The working electrode used in this cell was a rotating sheet, and the $TiSi_2$ was mixed with 15 weight percent Teflon 30 and water and then sprayed onto the sheet. after which it was sintered at 250°C for five minutes. The same electrolyte concentration and temperature were used as for previous tests. When nitrogen or hydrogen gases were used, they were bubbled through the electrolyte in the working electrode compartment. Methanol fuel was used at a concentration of 0. 1 molar.

The test results obtained are shown in Table II. As shown, the currents at 600 mv for both hydrogen and methanol oxidation with $TiSi_2$ are considerably higher than those obtained with the gold sheet, and these currents are significantly higher than the corrosion current of the $TiSi_2$.

TABLE II

Activity of $TiSi_2$ on Rotating Flag-Type Gold Current Collector for Hydrogen and Methanol Oxidation at a Potential of 600 mv

Electrode Material	Current for Nitrogen (μa)	Current for Hydrogen (μa)	Current for Methanol (μa)
Gold Sheet	-	<1	1. 1
$TiSi_2$ on Gold Sheet	2	16	4. 3

From the data obtained during this quarter, it can be concluded that $TiSi_2$ powder has some catalytic activity for hydrogen and methanol oxidation. Previous tests on sintered plugs of $TiSi_2$ detected no catalytic activity, but this is not surprising since the high temperatures used in sintering the powder would undoubtedly destroy the active sites.

The relatively high activity found previously for the silicides was apparently caused by platinum contamination from the counter electrode. The effect of the contamination differed among the silicides because some silicides are more amenable to platinum activation than others.

B. PRELIMINARY DATA FOR WSi_2

The electrochemical behavior of WSi_2 was investigated by the same procedure and at the same conditions used to study the silicides of titanium, molybdenum, vanadium, and tantalum. The potential sweep and steady-state (taken after maintaining the potential constant for 15 minutes) data for WSi_2 is shown in Figures 2, 3, and 4. As shown, there is essentially no difference between the curves obtained with solutions saturated with argon and those saturated with hydrogen. Further, the corrosion currents are approximately ten times those obtained with the titanium and molybdenum disilicides.

Subsequently, 2.8 μg of platinum was added to the WSi_2 electrode by adding the platinum to the solution and holding the electrode at -600 mv for 30 minutes. Triangular potential sweeps were made between -600 mv and 1100 mv at rates of 34 mv/sec and 100 mv/sec. As in the case of $MoSi_2$, the overvoltage in the hydrogen evolution region was reduced, but no activity for the oxidation of hydrogen could be observed. The magnitude of the corrosion current was not reduced significantly by the addition of platinum. No attempt has been made to activate the electrodes by depositing the platinum over a gold deposit.

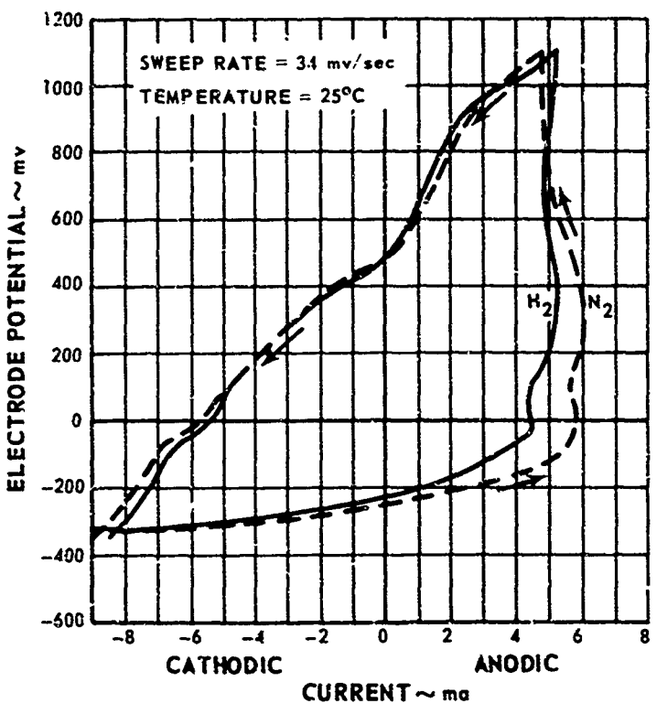

Figure 2 Triangular Potential Sweep Curves for WSi_2 With Sweep Rate of 34 mv/sec

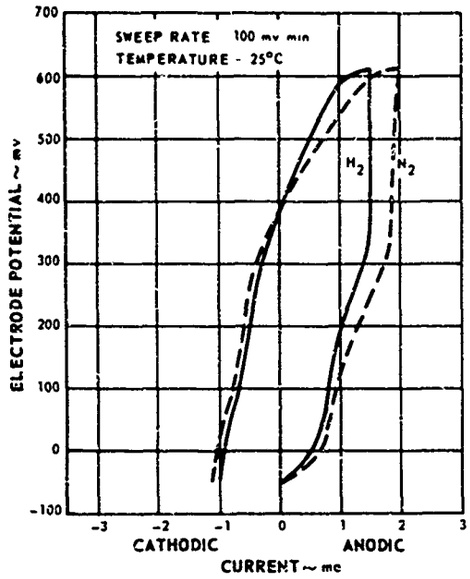

Figure 3 Triangular Potential Sweep Curves for WSi_2 With Sweep Rate of 100 mv/min

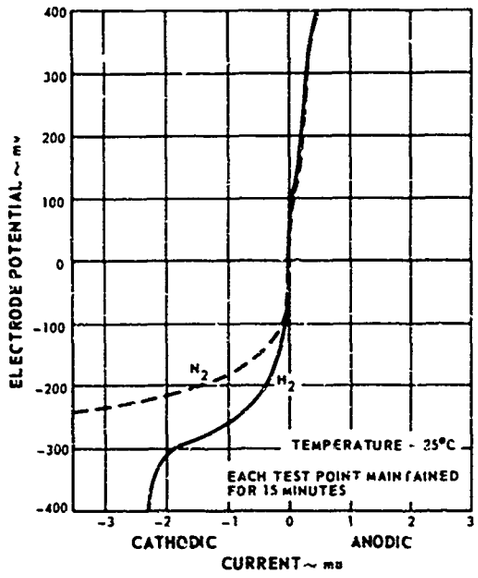

Figure 4 Steady-State Current-Voltage Characteristic for WSi_2

C. ELECTROCHEMICAL BEHAVIOR OF THE SILICIDES

Two studies were conducted to investigate the electrochemical behavior of the silicides in the absence of fuel. The first of these involved a correlation of crystal structure with behavior, and the second involved an experiment to determine the cause of the cathodic current observed at low positive potentials for $TaSi_2$ and VSi_2.

1. Effect of Crystal Structure on Electrochemical Behavior

During the course of the program, the electrochemical behavior of $TaSi_2$ was found to be similar to that of VSi_2, but quite different from that of $TiSi_2$ or $MoSi_2$. Since the structures of $TaSi_2$ and VSi_2 are the same, it was postulated that the similarity in electrochemical behavior was related to the crystal structure. Both VSi_2 and $TaSi_2$ have hexagonal structures; $MoSi_2$ and WSi_2 have tetragonal structures, and $TiSi_2$ has an orthorhombic structure. $TiSi_2$ is built of close-packed layers of the type shown in Figure 5. The titanium atoms of successive layers fall above the points B, C, and D, respectively. Therefore, each atom has ten neighbors. Each titanium atom is approximately equidistant from ten silicon atoms, and each silicon atom is approximately equidistant from five titanium atoms and five silicon atoms. In the VSi_2 and $TaSi_2$ hexagonal structures, the repeating unit is comprised of only three layers instead of four, with the metal atoms of successive layers falling above the points B and D only. In the tetragonal structures of $MoSi_2$ and WSi_2, however, the repeating unit is comprised of only two layers, with the adjacent layers being displaced with respect to one another such that the metal atom of one layer falls above point B of the other. Consequently, the three structures form an interesting series, all being built from the same type of close-packed layer superimposed in the same way so that each atom has ten neighbors, but differing in the number of layers in the repeating unit.

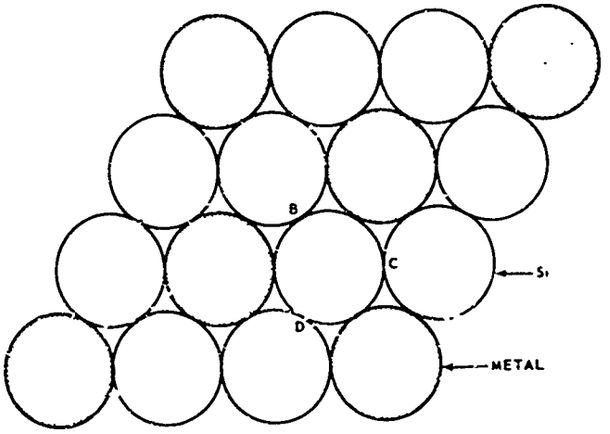

Figure 5 Crystal Structure of Silicides

From this analysis, it was concluded that the electrochemical behavior of WSi_2 should be similar to that of $MoSi_2$, the behavior of $TaSi_2$ should be similar to that of VSi_2, and the behavior of $TiSi_2$ should be different from that of either of the other two types of silicides. This is shown to be the case in the steady-state curves shown in Figures 6, 7, and 8. (These data were obtained by recording current readings after the corresponding potential had been maintained for ten minutes in a nitrogen-saturated electrolyte.)

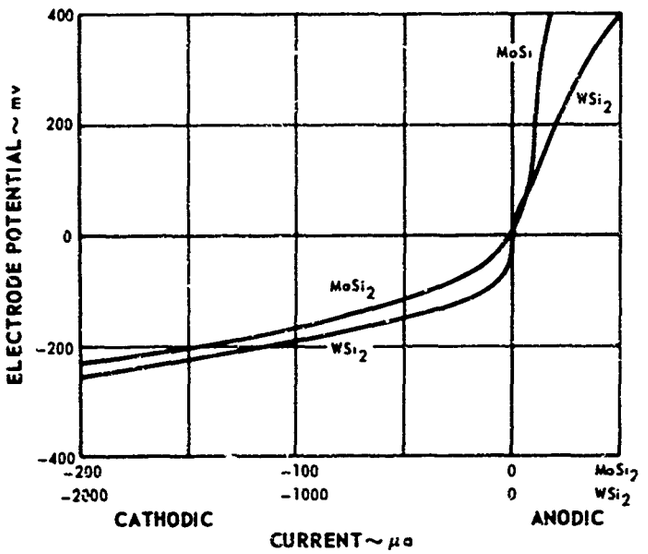

Figure 6 Steady-State Current-Voltage Characteristics for WSi_2 and $MoSi_2$

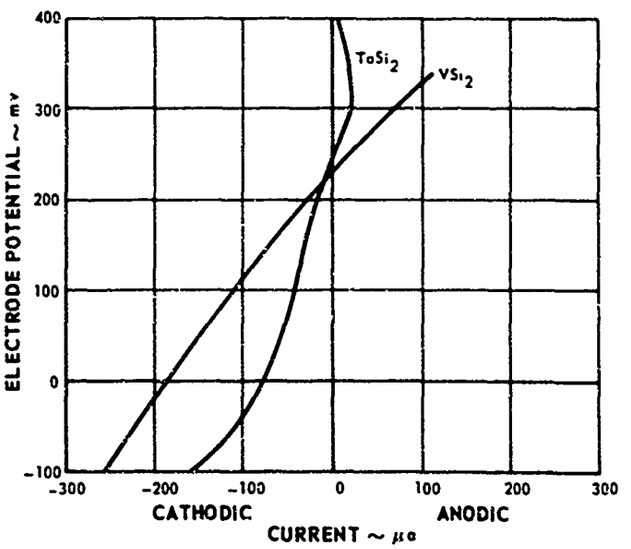

Figure 7 Steady-State Current-Voltage Characteristics for $TaSi_2$ and VSi_2

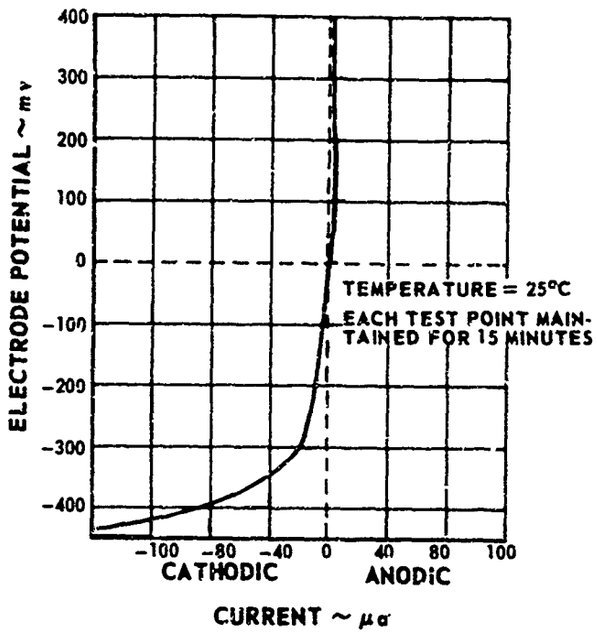

Figure 8 Steady-State Current-Voltage Characteristics for $TiSi_2$

2. Investigation of Cathodic Current of $TaSi_2$ at 100 mv

Both $TaSi_2$ and VSi_2 are characterized by cathodic current at potentials below 200 mv, and it was not known whether this current is caused by impurities or by the reduction of the oxide film. To find out, a rotating sintered $TaSi_2$ electrode was treated in 1-molar H_2SO_4 electrolyte at 25°C by maintaining a potential of 1200 mv for one hour. The cathodic current was then measured as a function of time at 100 mv. The electrode was then held at -1200 mv for one hour, after which the current was again recorded at 100 mv.

The results of the two tests are shown in Figure 9. As shown, pretreatment at 1200 mv was followed by an initial cathodic current of 1.3 ma at 100 mv which decayed relatively steadily and was still progressing after ten hours, when the test was terminated. This behavior is attributed to the reduction of the oxide formed at the more positive potential. After pretreatment at -1200 mv, the cathodic current remained constant at 0.22 ma. This behavior is difficult to explain in terms of oxide film formation, known reactions, or impurities and is not understood at this time.

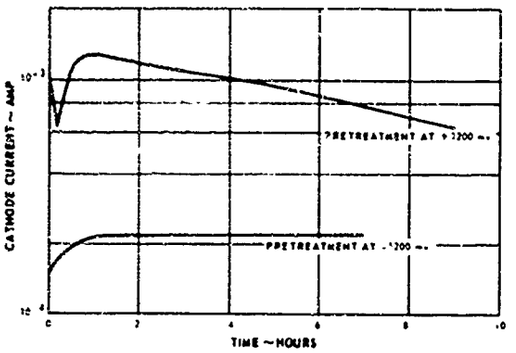

Figure 9 Effect of Prepolarization at +1200 mv and -1200 mv on the Cathodic Current of $TaSi_2$ at 100 mv

D. NOBLE METAL UTILIZATION ON $TiSi_2$

A series of experiments were performed to find a more quantitative measure of noble metal utilization on a silicide surface and to provide a baseline for judging the activity of surface-doped electrodes. The activity for hydrogen oxidation of smooth and platinized platinum electrodes of both the rotating flag and disk type was measured at the same conditions used for the silicide. Sweep curves were generated with a sweep rate of 34 mv/sec, and the results are shown in Figures 10 and 11. True surface area was determined by measuring the double-layer capacitance (assuming that smooth platinum has a double-layer capacitance of 40 $\mu F/cm^2$ true area) and by determining the hydrogen adsorption. The capacitance is determined from the curves by relating the current in the double-layer region to the voltage sweep rate. Hydrogen adsorption was determined by integrating the area under the sweep curve in the hydrogen adsorption region. The amount of charge involved for a theoretically smooth surface was calculated on the basis of the assumption that one atom of hydrogen is adsorbed on each surface platinum atom. The results of the area measurements normalized with respect to geometric area are shown in Table III.

TABLE III

Electrochemical Parameters for Rotating Disk and Flag-Type Platinum Electrodes

Electrode	Measured Double-Layer Capacitance ($\mu F/cm^2$)	Measured Hydrogen Adsorption (μ coul/cm^2)	Calculated Hydrogen Adsorption (μ coul/cm^2)	Surface Roughness (Real Area/Geometric Area) Double-Layer Capacitance	Surface Roughness (Real Area/Geometric Area) Hydrogen Adsorption
Disk (Smooth)	60	255	185	1.5	1.4
Flag (Smooth)	54	294	185	1.4	1.6
Disk (Black)	965	-	-	24	-
Flag (Black)	2500	10,600	185	62	57

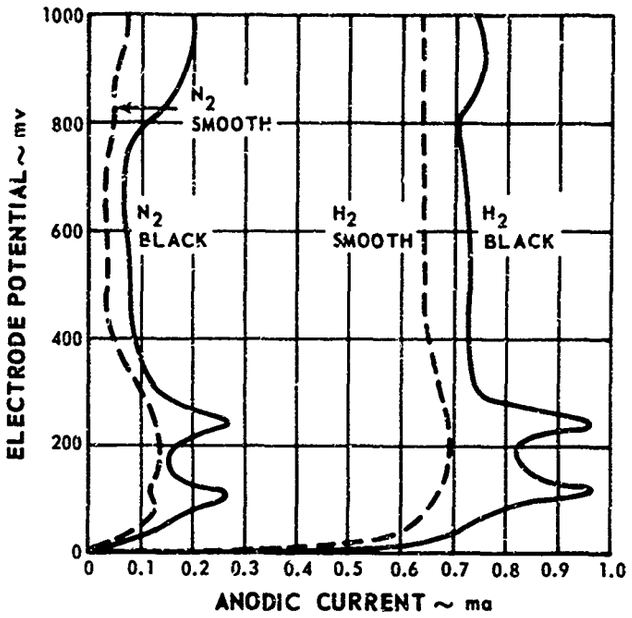

Figure 10 Anodic Branches of Triangular Potential Sweep Curves for Smooth and Platinized (Platinum) Rotating Disk Electrodes With Sweep Rate of 34 mv/sec

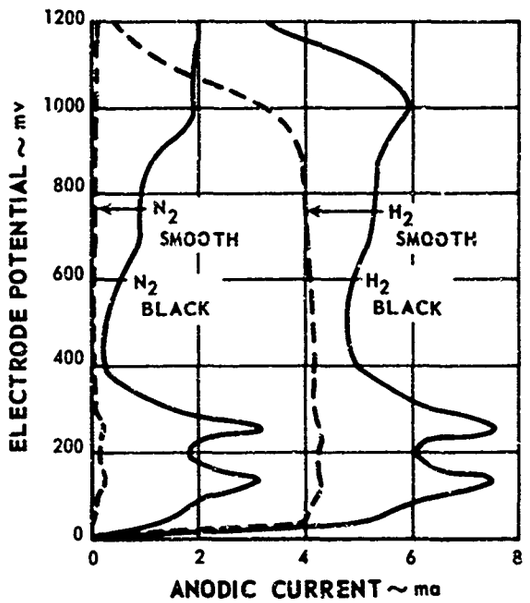

Figure 11 Anodic Branches of Triangular Potential Sweep Curves for Smooth and Platinized (Platinum) Flag-Type Electrodes With Sweep Rate of 34 mv/sec

The sweep curves (Figures 10 and 11) show that, in the case of hydrogen, the current in the limiting current region is not a function of the surface roughness, at least for a factor of 40 change in the roughness factor. This is to be expected in a mass-transport controlled process. Comparison of the limiting currents obtained with the disk and with the flag-type electrode reveals that the disk provides a higher limiting current by a factor of 1.5 for equivalent true areas.

From the limiting current on the rotating disk and from the fact that the current is limited by the geometry of the system, the amount of current which would be obtained from a geometrically flat monolayer of platinum having the dimensions of the disk can be calculated. This would represent complete utilization of the platinum for this system. For this calculation, it was assumed that the platinum forms in a square array for the first monolayer with an atomic radius equivalent to that calculated from the density. On this basis, a monolayer of platinum with an area of one square centimeter is equivalent to 0.36 μg, and, consequently, for the electrode disk size used, 0.12 μg would be required to form a monolayer over the disk surface, providing the surface is flat. Hence, if at least 0.12 μg of platinum is deposited as a monolayer on the surface of the silicide electrode, the limiting current should be 0.64 ma.

Comparison of this conclusion with the experimental results for platinum and platinum on gold deposited on $TiSi_2$ (see Figure 7 of the second quarterly report) does not verify the theory, however. Although the amount of platinum applied to the silicide exceeded the amount required to produce a monolayer over the geometrical surface area by a factor of about 10, the limiting current was 0.55 rather than 0.64 ma. This indicates that the utilization of the platinum is low, and, consequently, it is clear that it is not deposited in a monolayer, but rather in discrete islands. This would result in a simple geometrical area effect, reducing the diffusion current by the ratio of the area covered with platinum to the total area. In addition to this effect, the silicides have a relatively rough surface, which requires a larger amount of platinum to completely cover the surface. Hence, the lower limiting current for the silicide electrodes and the relatively large amount of platinum required seems to result from the combination of two factors which are inseparable until either the true surface area or the deposit crystallite size (or, complimentarily, the fraction of the substrate covered) is measured.

An attempt was made to measure the surface roughness of the $TiSi_2$ electrode by plating it with gold, since the double-layer capacitance of the resulting surface could be compared with that of a smooth gold sheet to calculate the relative surface area. The $TiSi_2$ electrode was cleaned by immersion in a HNO_3-HF mixture at 90°C for one minute followed by rinsing in distilled water. It was then placed for two minutes in a solution containing 1 g $KAu(CN)_2$, 2 ml 48 percent HF, and 100 ml H_2O, at room temperature. A shiny gold plate resulted. How-

ever, it was not possible to measure the double-layer capacity of the plated plug because the electrochemical behavior was the same as that of the unplated silicide. Apparently, the $TiSi_2$ plug is porous enough that the electrolyte penetrates into the structure.

E. EFFECT OF GOLD-PLATINUM RATIO ON $TiSi_2$ SURFACE DOPING

A series of experiments were reported in the second quarterly report in which $TiSi_2$ was plated from a sulfuric acid solution containing equal molar amounts of gold and platinum. The results were unusual since the sweep curve showed no defined limiting current and the maximum currents obtained were about 40 percent higher than the limiting current obtained for the rotating platinum disk.

During this report period, similar experiments were performed with co-deposits of platinum and gold, but the amount of platinum was held constant at 0.2 μg and the amount of gold was varied. The ratio of the current obtained for the co-deposit to that obtained for platinum is plotted in Figure 12 as a function of the weight percent of gold in the deposit. The curve exhibits maxima at 50 and 70 percent of gold which are higher then the level obtained with 0.2 μg of platinum alone. A sharp minimum occurs at about 55 percent of gold. There is some uncertainty in the absolute values of these percentages because of the small amount of the materials involved and because of the sharpness of the maxima and the minimum. However, a sufficient number of points have been repeated to assure that the general shape of the curve is correct and that the minimum occurs close to the indicated value. It is difficult to interpret these results because the character of the surface is not known, that is, it is not known whether the deposit is a mixture or an alloy. At present, an attempt is being made to correlate the results with those published by M. W. Breiter* on hydrogen adsorption on heterogeneous platinum-gold alloys.

* M. W. Breiter, Transactions of the Faraday Society, Vol. 61, p. 749, 1965

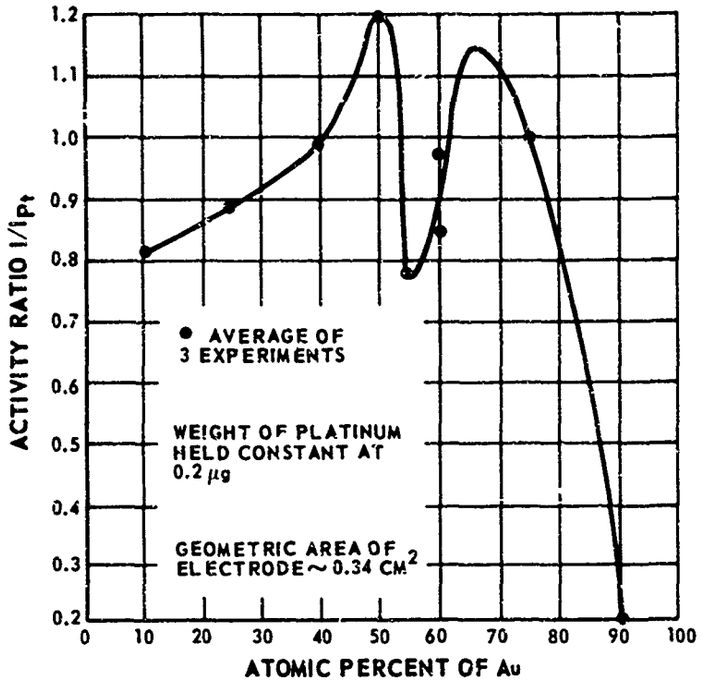

Figure 12 Activity for Hydrogen Oxidation of Platinum-Gold Co-deposit Relative to that of Platinum

III. CONCLUSIONS AND RECOMMENDATIONS

The experiments performed on $TiSi_2$ on a gold substrate indicate that $TiSi_2$ powder has a slight catalytic activity for hydrogen and methanol oxidation, whereas $TiSi_2$ in the form of a sintered plug has no detectable catalytic activity. This is not surprising since the high temperatures used during fabrication of the plug could destroy the active sites. The activity previously reported for the silicides on a gold-plated platinum current collector is probably caused largely by the small amount of exposed platinum on the current collector rather than by the silicide. Further, since corrosion testing was usually performed first, some of the exposed platinum could dissolve in the electrolyte at the high potentials used and subsequently plate out on the silicide at lower potentials. The higher catalytic activity observed during testing conducted prior to the contract apparently was caused by plating of the silicide with platinum from the platinum counter electrode used at that time.

The electrochemical behavior of the silicides in the absence of fuel was found to be related to crystal structure. VSi_2 and $TaSi_2$ have hexagonal structures and similar electrochemical characteristics. Similarly, WSi_2 and $MoSi_2$ both have tetragonal structures and also have similar electrochemical characteristics, but different characteristics from those of VSi_2 and $TaSi_2$.

Surface doping of $TiSi_2$ with platinum and with platinum-gold combinations by electrodeposition from very dilute solutions of gold in sulfuric acid results in low utilization of the noble metal. No evidence was found that the silicide made any significant contribution to the catalytic activity observed under these conditions. Since no catalytic activity on the part of the silicides has been observed, it is recommended that further studies of silicides be abandoned. The use of silicides solely as catalyst supports does not appear to be desirable because of the difficulty in obtaining silicides in a finely divided state and because, in the finely divided state, they have a high electronic resistance because of the high ratio of oxide volume to silicide volume.

Tests have indicated that platinum contamination of the current collector can seriously distort the results. The amount of platinum responsible for the activity observed on gold in Figure 1 is not known, but it must be present in very small amounts. Consequently, some of the data published in the literature on electrodes other than platinum is questionable, since most workers have used platinum as a counter electrode. An even more serious source of platinum contamination would be the fairly standard practice of conducting pre-electrolysis of the electrolyte using platinum electrodes. The resulting contamination of the electrolyte with platinum and its subsequent deposition on the electrode under study could seriously affect the results.

Because the platinum contamination is of considerable significance to the study of electrocatalysis and since the silicides have been found to be unsuitable as catalysts for hydrogen or methanol reduction, it is recommended that the remainder of the contract effort be devoted to the study of the effect of trace amounts of platinum on a gold substrate. It would be of interest to determine how small an amount of platinum can be detected on gold by electrochemical techniques, and it would also be of value to determine how the surface coverage of gold with platinum affects hydrogen adsorption and the Tafel parameters for hydrogen evolution and dissolution.

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13 ABSTRACT

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Electrochemical Catalysis		4				
Hydrogen Oxidation		4				
Methanol Oxidation		4				
Silicides		1				
Corrosion		1				

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