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FUNDAMENTALS OF THE OXIDATION PROTECTION OF COLUMBIUM AND TANTALUM

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By

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Foreword

This is the fourth semiannual report on NASA Grant No, NGR 33-013-017, It covers work from April 1, 1967 to October 1, 1967.

The first two reports were issued March 31, 1966 and October 1, 1966 and had limited distribution, The third report, accordingly contained a comprehensive review of the entire program and was issued April 1, 1967,

This grant was made by the NASA Office of Grants and Research Contracts. The NASA Technical Monitor is Mr. Robert E, Oldrieve of the Lewis Research Center, Cleveland, Ohio. The work is under the supervision of Professors Morris Kolodney and Robert A. Graff and is being performed by Mr. Stanley R. Levine, Mr. Andrew G. Mueller, Mr. Leon Schwartz and Mr, Frederic N. Schwettmann who are graduate students at The City College of New York.

Summary

An investigation of the fundamental processes involved in the protection of tantalum and columbium by their silicides is in progress. The program has four parts. The first part is devoted to establishing thermochemical data for the silicides and employs an entirely solid state electrochemical cell. The second part deals with the protection of both coating and substrate by the protective glass formed during oxidation. Under certain conditions of temperature and pressure this glass does not form and the coating fails. The study of glass structure and growth is aimed at understanding the causes of failure and providing a rational basis for improving coatings. In the third part oxidation rates and the possibility of using coating modifiers to promote the formation of glassy films is to be tested. Lastly, since coating life may be limited by the formation of intermediate phases between the silicide and the substrate, these interactions are being investigated in the fourth part of the program along with the efficacy of diffusion barriers to retard intermediate phase growth.

In all cases the silicides, with any required additives, will be used in bulk form. Disks are fabricated by cold pressing and sintering. These methods have been developed, and specimens of over 90% theoretical density have been consistently obtained.

The previous report described the development of specimen fabrication techniques, the design and construction of equipment and preliminary tests of some of the methods to be used. Further tests and improvements in methods and apparatus are given in this report.

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Introduction

Refractory metals are required for a variety of applications at elevated temperatures, particularly for air-breating engines, because their high strength is retained under service conditions. These metals, however, suffer from a susceptibility to oxidation. Above about 1300°F oxidation rates are prohibitive, and a protective coating is required. Silicide and aluminide coatings have been most successful thus far.

The development of coatings has proceeded by largely empirical methods. While this is undoubtedly the way to obtain practical coating systems rapidly, a successful coating technology must be backed by fundamental information atmosphere-coating-substrate systems. Previous studies on the development of protective silicide coatings were received in the third Semiannual Report,

The program reported here was undertaken to provide an understanding of the behavior of the coated substrate in its environment. This involves the mechanisms and rates of oxidation of the coating and the effects of modifiers as well as the mechanisms and rates of interaction of the coating with the substrate. The tantalum-silicon and columbium-silicon systems, at temperatures up to 2500°F and under oxygen pressures of one atmosphere and above, are under study.

Four major lines of investigation are in progress:

1) thermochemical data,
2) glass structure and growth,
3) oxidation rates and coating modifiers,
4) substrate-coating interaction and barriers.

To discuss the behavior of tantalum-silicon and columbium-silicon systems under oxidation requires thermochemical data for the oxides and silicides, At present the free energies of formation of the silicides of tantalum and columbium are not available.

These are being determined in the first part of the program using a solid galvanic cell at elevated temperature,

The oxidation protection of metals by silicides depends on the formation during oxidation of a glass which acts as a barrier to oxygen. The oxidation products frequently do not form a protective film. In the second line of investigation the glasses formed on oxidation are being investigated with the objective of understanding the differences between the structure of protective and nonprotective films and the processes controlling their growth. This understanding will provide a rational basis for improving the protectiveness of coatings.

The possibility of using modifiers to improve the structure of the film is being investigated in the third part of this program. Substances which form stable oxides or silicates may be expected to increase coating life and a number of these will be tested.

In the fourth phase of the project the interaction of the coating with the substrate is being studied. This interaction produces an intermediate silicide incapable of forming a protective film. The rate of growth of the intermediate phase may thus determine coating life. These phases grow by diffusion, and the use of barriers to slow the growth of the intermediate has been reported.

Thermochemical Data

Presently available thermodynamic data for tantalum and columbium silicides are limited to heats of formation obtained calorimetrically (Robins and Jenkins (1)), by Knudsen effusion (Myers and Searcy (2)), or by reaction equilibria (Brewer and Krikorian (3)). The average accuracy of the best available data is about ± 15%. To date there have been no experimental determinations of the free energy and entropy of formation of these silicides. The free energy of formation of these compounds can only be estimated from heat of formation data under the assumption of a zero entropy of formation.

In this investigation the free energy of formation of the tantalum silicides are being determined from EMF measurements on electrochemical cells of the form:

Pt/silicide electrode//oxide electrolyte//Ta, Ta_2O_5/Pt (1)

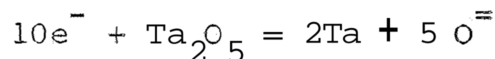
where the free energy of the reaction is given by

$$\Delta F_R = -nFE \qquad (2)$$

and ΔG_R contains the known free energies of formation of β -quartz and β - Ta_2O_5 and the unknown free energies of formation of the silicides. The same is true of the entropy of the cell reaction which is proportional to the temperature derivative of the voltage,.

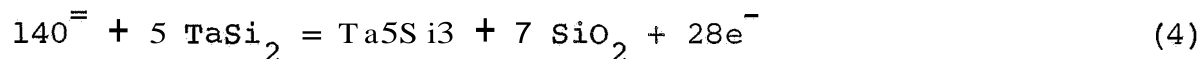
$$\Delta S_R = nF \left(\frac{\partial E}{\partial T}\right)_P \qquad (3)$$

The reference electrode half-cell reaction is:



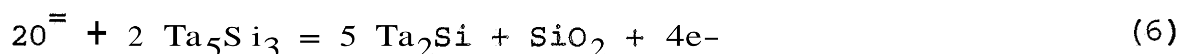
$$10e^- + Ta_2O_5 = 2Ta + 5\,O^{=}$$

The expected reactions at the silicide electrodes, which in each case is composed of the participating reactants and products, are:

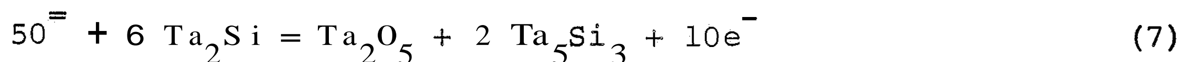


$$14O^{=} + 5\ TaSi_2 = Ta_5Si_3 + 7\ SiO_2 + 28e^{-} \qquad (4)$$

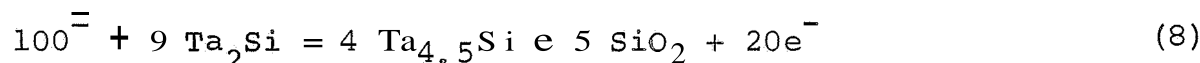
$$35O^{=} + 4\ Ta_5Si_3 = 7\ Ta_2O_5 + 6\ TaSi_2 + 70e^{-} \qquad (5)$$



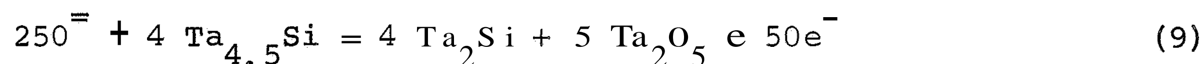
$$2O^{=} + 2\ Ta_5Si_3 = 5\ Ta_2Si + SiO_2 + 4e^{-} \qquad (6)$$



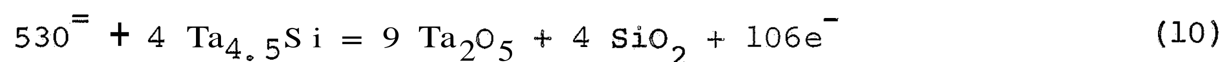
$$5O^{=} + 6\ Ta_2Si = Ta_2O_5 + 2\ Ta_5Si_3 + 10e^{-} \qquad (7)$$



$$10O^{=} + 9\ Ta_2Si = 4\ Ta_{4.5}Si + 5\ SiO_2 + 20e^{-} \qquad (8)$$



$$25O^{=} + 4\ Ta_{4.5}Si = 4\ Ta_2Si + 5\ Ta_2O_5 + 50e^{-} \qquad (9)$$



$$53O^{=} + 4\ Ta_{4.5}Si = 9\ Ta_2O_5 + 4\ SiO_2 + 106e^{-} \qquad (10)$$

During the past six months the major effort has been a thorough shakedown of the apparatus (Fig, 1) and the incorporation of improvements. A series of cells with known EMFs covering a wide range of oxygen chemical potentials was investigated. The results of some of these experiments are given in Table I,

Cells I and III where both electrodes have high oxygen partial pressures gave stable, reproducible, and accurate results. The observed EMFs were independent of the argon flow rate, Cells II, IV, V and VI where one or both electrodes have an oxygen partial pressure gave EMFs which were unstable and for the most part inaccurate, The EMFs listed for these cells are not representative but indicate that the technique is of potential usefulness at low oxygen partial pressures. The EMFs listed were observed for short periods of time (several minutes), For the major part of any experiment, these cells gave inaccurate EMFs which were very sensitive to argon flow rate and temperature changes.

Table I. E.M.F. Measurements

Cell	Temperature °C	EMF mv	ΔF(T) or Expected EMF	% Error
I) Pt/Ni, NiO//ZrO_2 - 7.5 wt% CaO//Cu, Cu_2O/Pt	596	285.2	F_{298}=15060 for the cell reaction	+0.6%
	602	283.8		
	648	281.4		
	654	280.1		
	698	276.3		
	748	272.2		
II) Pt/Ta, Ta_2O_5//ZrO_2 + 7.5 wt% CaO//Ni, NiO/Pt crucible	700	885	EMF 890	−0.[illegible]%
III) Pt/Fe, Fe_xO//ThO_2 + 15 wt% Y_2O_3//Ni, NiO/Pt sintered pellet	595	245.2	245.9	−0.7%
	608	245.1	247.0	
	696	255.2	256.0	
	702	254.8	256.8	
	726	257.7	259.3	
	791	262.7	265.9	
	826	268.0	269.4	
	909	270.9	274.2	
	976	276.4	278.2	
IV) Pt/Ta, Ta_2O_5//ThO_2 + 15 wt% YaO_3//Cr, Cr_2O_3/Pt sintered pellet	892	158.4	151.0	+4.6%
V) Pt/Ta, Ta_2O_5//ThO_2 + 6 wt% Y_2O_3//Cr, Cr_2O_3/Pt sintered pellet	895	158	151.5	+4.3%
	890	155	151.4	+2.4%
VI) Pt/Ta, Ta_2O_5//ThO_2 + 6 wt% Y_2O_3//Cr, Cr_2O_3/Pt sintered pellet	906	153.6	151.6	+1.3%

The difficulties encountered with these cells were believed to be caused by one or more of the following: a parallel electrical circuit; electronic conduction in the electrolyte; electronic conduction via a parallel reaction in the gas phase; insufficiently pure argon as a result of leakage in the system or an inadequate purification train; and finally, poor contact at the electrode-electrolyte interfaces which results in a mixed potential,

Steps were taken to eliminate each of these possible difficulties. Teflon lead-throughs were substituted for the ceramic lead-throughs and impedance measurements were made at room temperature and 800°C without the presence of a cell and under open and closed circuit conditions. The impedance of the parallel path was high enough to present no difficulties,

According to available information in the literature on oxide electrolytes ThO_2 - 6 wt% Y_2O_3 is one of the best choices for EMF measurements at low oxygen partial pressures, These electrolytes were, therefore, fabricated from 99.9% ThO_2 and 99.99% Y_2O_3 powders. The powders were weighed out in the proper proportion, mixed and pressed into ½" diameter by 1/8" high pellets under 40,000 psi, The pellets were sintered in vacuum for three to four hours at temperatures from 1950°C to 2150°C. Typical density values for 3½ hour sintering times are 87% of theoretical at 1950°C; 91% at 2050°C and 90.5% at 2150°C. The sintered pellets are then ground on a diamond disc and lapped to a mirror finish on a nylon cloth with a levigated alumina abrasive. The sintered pellets have a dark olive green color believed to be caused by oxygen in excess of the stoichiometric amount, They turn white when exposed to the low oxygen partial pressure of the cell. No major improvement in results was realized from these electrolytes.

An attempt was made to reduce any existing parallel gas path by incorporating a charged particle collector into the cell design,

This was accomplished by placing a nickel collar with a positive bias in the vicinity of the cell, Biases of up to 40 volts were used with no detectable effect on the observed EMFs.

The system was checked for leaks prior to runs V and VI with a portable vacuum pumping station, Some leaks were found and eliminated. A vacuum valve was added to the permanent vacuum line,

Contact between the electrodes and the electrolyte was improved in cell VI as compared to cell V and other preceding runs by carefully grinding and polishing all faces of the electrodes and electrolyte, The thickness varied by no more than 0,002 inches on any diameter of any of the three pellets and by no more than 0,0010 inches on the assembled cell, The cell was loaded by a lever capable of producing up to 250 psi on the cell, The results for cell VI were better than for any prior run with electrodes exhibiting low oxygen partial pressures, The listed result was observed for nine minutes, At the end of this period the electrometer and the potentiometer were balanced, Upon resumption of the measurement the voltage declined rapidly,

The final improvement incorporated into the system was a second gas purification train, This apparatus consists of a drying column loaded with anhydrous magnesium perchlorate, a Zr - 12.5 wt% Ti getter column and a tantalum getter column. The latter column can be bypassed, The entire system can be used independently or in series with the old purification train, The apparatus with the modifications outlined above is shown in Figure 2,

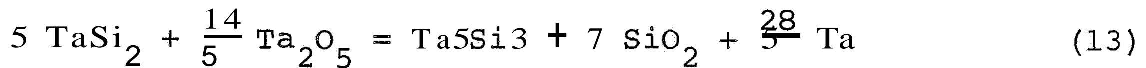
The entire system (old gas train, new gas train and cell) was checked for leaks after being loaded with the cell:

$$Pt/TaSi_2, Ta_5Si_3, SiO_2//ThO_2 - 6 \text{ wt\%} Y_2O_3//Ta, Ta_2O_5/Pt \qquad (11)$$

The apparatus was held under vacuum for twenty-four hours. The argon was then started and the Z_r - 12 wt% Ti getters were brought up to temperature. The first column was operated at 425°C and the second at 375°C. The system was purged for 24 hours, The cell was then heated to 800°C. The cell exhibited the usual initial behavior. The voltage reached a positive maximum, declined and changed sign. After about two hours at temperature the voltage became positive again. This behavior is due to a transient process in the cell. The electrolyte initially contains excess oxygen which is responsible for the greenish hue of these materials in the as-sintered condition. During the initial period of operation the excess oxygen is removed. Oxygen removal from the electrolyte in conjunction with the cell reaction results in a mixed potential, The results of this experiment are presented in Table II. They fit the following equation:

$$E = -208.4 + 0.1974T \pm 4.7 \text{ mv} \qquad (12)$$

Since the cell reaction is:



$$5\ TaSi_2 + \frac{14}{5} Ta_2O_5 = Ta_5Si_3 + 7\ SiO_2 + \frac{28}{5} Ta \qquad (13)$$

equation (12) may be rewritten in terms of free energies of formation of the silicide pair:

$$\Delta F^{(T)}_{Ta_5Si_3} - 5\ \Delta F^{(T)}_{''} \qquad 6,530 - 148.63T + 4860 \text{ cal} \qquad (14)$$

Table II

E.M.F. Values for Cell of Equation 11

Temperature	EMF	Length of time observed
910°C	21.9 mv	24 min.
893°C	20.1 mv	60 min.
1000°C	50.9 mv	24 min.
914°C	21.9 mv	12 min.
813°C	7.2 mv	12 min.
1002°C	42.0 mv	6 min.
818°C	7.8 mv	12 min.

During the next few months the other cells outlined in equations (5) through (10) will be investigated and the free energies of the individual silicides will be determined,

Glass Structure and Growth

The object of this phase of the program is to determine the mechanism of protective film formation by evaluating the structure, composition and growth rate of the oxide film.

In order to clearly establish the intrinsic oxidation behavior of the coating materials, their oxidation is being studied in bulk form. This approach to the coating problem is particularly attractive in that it eliminates the physical problems found in coatings, and also allows the effects of small amounts of additives to be determined. Pure $TiSi_2$, which upon oxidation forms a protective oxide film, is the initial material being considered. When the mechanism of protection for this material is established, the effect on the oxide film of the addition of silicon and $TaSi_2$ to the pure $TiSi_2$ will be considered.

Wafers of the silicides are prepared by the techniques of powder metallurgy. The initial oxidation studies are carried out in static air in a box-type furnace. Techniques for evaluating the character of the film are being developed using these preliminary specimens. Final oxidation experiments are performed in a tube-type furnace with controlled atmospheres. These studies establish the effect of temperature, oxygen pressure and wafer structure on the character and growth rate of the oxide film. Oxidation mechanisms will then be formulated.

Experimental Sample Preparation

Pure $TiSi_2$ wafers with a density 95% of theoretical have been prepared using powder metallurgy methods. The procedure consists of mixing the disilicide powder with binder, pressing, presintering, sintering, grinding and polishing. In a recently purchased Brew furnace, 4 wafers can be sintered simultaneously. At an uncorrected temperature of

$1400^{o}C$ as determined by an optical pyrometer, density variation among the 4 samples is from 95-97% of theoretical when sintered for 15 minutes. Accurate temperature control during the sintering of $TiSi_2$ is important. When the sintering temperature is $1375^{o}C$, the range of densities is 92-94% of theory, while at $1425^{o}C$, melting occurs. Since the melting point of $TiSi_2$ is reported at $1550^{o}C$, there is considerable error in the present readings, Corrections for the temperature reading are being developed.

Preparation of the sintered wafer for oxidation consists of grinding successively on 220 grade, 30 micron, 15 micron, and 9 micron diamond disks, followed by lapping with 6 and then 3 micron diamond paste. Final polish is with 0.05 micron gamma alumina micropolish.

Analytical Techniques

The suitability of several analytical techniques for determining the character and growth rate of the oxide film has been investigated. While infrared and X-ray analysis appear to yield valuable information on the character of the film, the VAMF'O technique for determining film thickness (4), appears to be unsuitable.

In the use of the X-ray technique, part of the oxide film is removed from the substrate. This is accomplished by drilling a small hole approximately 3/4ths of the way through the sample. The wafer is then exposed to chlorine at about $800^{o}C$. The silicide reacts to form volatile chlorides while the oxide is untouched. The oxide window formed is then removed and powdered for analysis.

In the infrared analysis, a Perkin-Elmer ATR unit has been modified to operate like a simple reflectance unit. Infrared spectra from 2.5 to 40 microns are being obtained on a Perkin-Elmer 621 spectrophotometer.

Considerable ordinate scale expansion is required to obtain suitable absorption peaks.

The unsuitability of the VAMFO technique for determining film thickness is due primarily to the non-homogeneous character of the oxide film. This results in scattering of some of the incident light which, in turn, makes it difficult to observe the position of the maxima and minima interference fringes. The film does, however, fulfill some of the requirements for optical film thickness determinations. This was demonstrated by observing the film on a reflectance attachment in a UV spectrophotometer. Maxima and minima due to interference were clearly observed. If the refractive index of the film in this wavelength region were known, the technique could be suitable. This assumes that the thickness is uniform and also that the transparent part of the film is of uniform composition. The UV and other thickness techniques will be reconsidered as more information is developed on the composition of the film.

Micrographs of the oxide surface are being prepared,

Oxidation Furances

Three globar-heated, vertical tube-type oxidation furnaces have been constructed and tested, The inner furnace shell is constructed from JM 3000 firebrick rated at 3000°F, while the outer layer is made with JM 2600 firebrick. The furnace heating chamber is 4" x 4" x 19". Heating is accomplished by four 1/2" diameter globar heating elements. The elements are connected in series and are spaced symmetrically around the center of the furnace, A Mullite tube is used to contain the specimens.

Furnace 1 has been set up for oxidation studies at temperatures up to 2000°F. Temperature control is with a Leeds & Northrup Series 60 two action D.A.T. control unit in a Speedomax H recording controller, With this unit, temperature variation is ± 5°F. The two additional furnaces are designed for studies in the range 2000-2500°F.

A sample holder for studies up to at least 2000°F has been constructed. It is made of Vitreosil (fused silica) and is shaped to hold four specimens over a heating length of 4 inches. Testing at 2000°F for 100 hours indicates that the silica does not lose its strength, devitrify or react with the sample.

Furnace number 1 was tested by oxidizing two pure silicon wafers at 1832°F for 45 hours. Lapped wafers were treated with a chemical polish (45 HF.75 HNO_3 . 45 HAc) for 30 seconds to improve the surface quality. They were placed at opposite ends of the Vitreosil sample holder and lowered into the furnace. An earlier approximate temperature profile indicated a 10°F variation over the length of the sample holder. Weight changes were recorded by a Mettler microbalance and oxide film thickness was determined by interference color charts (4). The oxidation rates for the wafers were within 5-10% of each other and on the average within 5% of published literature values. Precision should be improved with the $TiSi_2$ wafers since larger weight gains will be observed.

Oxidation Experiments

In a preliminary study aimed at determining the nature of the oxide film that will be obtained, three polished wafers of pure $TiSi_2$ were oxidized in static air in a Lindbergh box furnace at 1500, 1900 and 2400°F. The sample at 1500°F exhibited a weight gain of only 0.1 mg/cm^2 after 67 hours of oxidation. This is equivalent to that

obtained on oxidation of pure silicon which forms an extremely impervious SiO_2 film. At 1900°F, a weight gain of 0.4 mg/cm^2 was obtained after 84 hours, while at 2400°F, the weight gain was 1.4 mg/cm^2 after 96 hours. In all cases, the oxidation was parabolic with little weight change being observed after the initial 40 hours.

Micrographs of the oxide films formed on oxidizing $TiSi_2$ are shown in Figures 3 to 6. In the 1500 and 1900°F samples, three distinct phases, labeled α, β and γ are clearly observed. Previous X-ray studies on similar samples indicated that TiO_2 (rutile) was the only crystalline material present. An infrared spectrum obtained with a reflectance attachment on a Perkin-Elmer 621 spectrophotometer showed absorption peaks, characteristic of Si-0 vibration at 1060 cm^{-1} and 785 cm^{-1} (4). TiO_2 (rutile) is known to have a strong, broad absorption band from 600 to 700 cm^{-1} (6). This was not observed in the spectrum of the oxide films.

When these analytical results are compared with the micrographs of the specimens, a reasonable interpretation can be made. The dark areas labeled α (yellow-brown) appear to be crystalline TiO_2 (rutile). The light β areas are probably pure $Si8_2$ (amorphous). For the 1500°F specimen, each grain-like area is actually a different color, mostly violet and yellow with a few green areas. In the 1900°F sample, this area is almost entirely green. In all cases, the colors appear transparent as do $Si0_2$ films grown on silicon. The different colors may be due to a difference in film thickness. Interference patterns were obtained on the 1900°F specimen with a UV spectrophotometer. If the amorphous part of the film is assumed to be pure SiO_2, the thickness can be approximated as follows (7):

$$t = \frac{M}{2(n^2 - \sin^2\theta)^{1/2}} \cdot \frac{\lambda_1\lambda_2}{(\lambda_1 - \lambda_2)}$$

where:

M = number of fringes between two maxima

n = refractive index

θ = angle of incidence

λ_r = wavelength of maxima

In this case:

$M = 2$

$n = 1.50$ (for pure SiO_2)

$\theta = 45^o$

$\lambda 1 = 0.328$ microns

$\lambda 2 = 0.247$ microns

which gives

$$t = \frac{2}{2(1.50^2 - \sin^2 45)^{1/2}} \cdot \frac{(0.328)(0.247)}{(0.328 - 0.247)}$$

$\therefore$

$t = 0.76$ microns

The film thickness can also be estimated from the color of the film, again assuming it is SiO_2. A green SiO_2 film can have a thickness of 0.55, 0.72 or 0.93 microns depending on the interference order. The value 0.72 would appear to confirm the value obtained by the W

interference method. However, a pure silicon wafer oxidized at the same conditions would give a thickness of 0.88 microns (5). The $TiSi_2$ wafer would probably give rise to a thicker oxide film at comparable operating conditions. The only conclusion that can be drawn from these results is that the oxide film thickness is in the region 0.7 to 1.0 micron.

The third area in the micrograph, γ , appears to grow at the oxide grain boundaries. This may be a titanium silicate.

Figure 6, a micrograph of the specimen oxidized at $2400^{o}F$, indicates a different mechanism at this temperature. Analysis of this film is in progress.

Oxidation Rates and Coating Modifiers

The work described in the previous section was concerned with providing fundamental understanding of glasses formed in silicide oxidation by analyzing the protective and non-protective glasses. At the same time, it is possible to attempt synthesis of protective glasses on the basis of existing principles for glass formation, The technique of manufacturing wafers by powder metallurgy methods lends itself readily to the introduction of modifiers. The composite material may then be evaluated by oxidation rate studies to determine the degree of success.

The previous report outlined guidelines whereby the principles of glass formation might be applied to the development of protective glasses. Since then an extensive literature search has been performed. Fundamentals of glass theory and practice, along with information on tantalum-bearing glasses was sought. This search was recently completed, and has shown promising directions for future research.

Missing from the literature are useful data for the $Ta_2O_5 - SiO_2$ system. Nowotny, et al.[8] suggested the existence of a $Ta_2O_5 - SiO_2$ glass as the oxidation product of a 70 atom% Ta, 30 % Si (approximating $TaSi_2$) alloy. Janakirama - Rao[9] claimed to have produced glasses of 95 - 99.9% SiO_2, 5-0.1% Ta_2O_5, by weight. These glasses exhibited thermal expansions less than that of fused silica. Thus, the starting point for this research is the verification of the above glass range and the investigation of higher tantala contents.

Another important piece of information not found in the literature is the phase diagram of the Ta_2O_5-SiO_2 system. Armstrong, et al.[10] reports that mixtures, corresponding to 8 and 20 wt.% Ta_2O_5, melt at $1590 \pm 10^{\circ}C$. These two eutectic compositions were thought to perhaps straddle a miscibility gap. This rather limited gap seems unlikely, and either a larger gap, or a compound should appear after the first eutectic composition. The compositions themselves are subject to error, since both TaO and TaO_2 are highly volatile at the test conditions ($1650^{\circ}C$, 10^{-7} atm.). Glasser, et al.[11] present a method for predicting miscibility gap based on the ionic potential and a "valence correction" for the cation introduced along with silica. Ionic potentials above and below 3 are seen to lead to two distinct types of liquid immiscibility melting.

The Ta-O bond, in contrast to the Si-O bond, is more ionic (63% compared to 51% ionic). This undoubtedly introduces a Frenkel or fissured character to the melt. A clustering of tantala-rich material of increased order, set in a matrix of highly mobile silica-rich material is expected. De Vries et al.[12], in observing TiO_2-SiO_2 glasses, noted clear glass mounds of silica-rich liquid along with devitrified masses (yellow to brown) of titania-rich liquid, It was concluded that titanium partly decreases in coordination from 6 to 4 at high temp-

eratures. This might also occur with tantalum, depending on temperature and the influence of neighboring cations. Ta^{5+}, because of its larger size and charge, is more likely to appear interstitially. Accordingly, electrostatic bonds between Ta^{5+} and O^{2-} are much stronger. Long-range Coulombic interactions result, which tend to reinforce and tighten the network (packing effect).

The primary object of this research is to improve the glass forming ability of tantala in silicate systems. Modifiers, have been selected to do this. The idea of replacing two Si^{4+} ions, with a $X^{3+} - Y^{5+}$ couple seems to be the most promising. Grimm and Huppert [13] used the couple $Al^{3+} - P^{5+}$ to synthesize aluminophosphate glasses and found that the liquidus temperature was raised 300°C. The couples $Al^{3+} - Ta^{5+}$ and $B^{3+} - Ta^{5+}$ seem to be the most appropriate choices. Other candidate modifiers are Ti^{4+}, V^{5+} and Zr^{4+}.

Methods of producing glasses are being explored. Direct resistance and induction heating apparatus are available. A simple but effective method, capable of high temperatures, consists of melting very small quantities (10-20 mg.) in a U - or V - shaped kink in a resistance heated Pt alloy wire [14]. Simple switching off of the heating current results in an extremely rapid quench, since the quantity and surface area of the melt is small compared to air bath environment. Potential crucible materials for melting glass batches are fused silica, alumina, platinum and its alloys, tantalum, and tungsten.

Three basic means of examination and identification will be used. They are metallographic inspection, X-ray diffraction and infra-red spectroscopy.

Substrate-Coating Interaction and Barriers

The service lifetimes of disilicide coatings are shortened because they interact by diffusion with the metallic substrates to form lower silicides, such as Ta_5Si_3. The latter are unable to form the protective glassy oxide, presumably because of the simultaneous formation of the substrate metal oxide. Therefore, an understanding of the mechanism of growth of the lower silicide layer and its inhibition is an important approach to increasing the coating life.

The general approach consists of bringing wafers of the substrate metal and coating material into contact under pressure at the elevated temperatures of interest. The rates of growth of the intermediate silicides will be measured. At the same time, marker experiments will be performed to determine the relative rates of diffusion of metal and silicon, The same techniques will then be applied to measure and explain the performance of additive or barrier elements such as titanium and chromium.

During the past six months equipment construction was completed, tantalum disilicide wafer preparation was put on a mass production, basis and five trial runs were made with diffusion couples,

Two furnaces for annealing the diffusion couples, together with temperature control and argon flow, where completed and tested. All controls, as well as the device for raising and lowering the couple from the hot zone, are now operating satisfactorily. Temperature control is within $\pm 5^{\circ}F$. Oxidation of specimens during a run, due to the small amount of oxygen in the argon, can be reduced by the use of a tantalum getter enclosure.

Tantalum disilicide wafer production is now at the stage where an average of 8 to 10 sintered wafers are produced per day from one sintering furnace. $TaSi_2$ is synthesized in 60 gram batches, and ground and mixed with the sintering aide (0.5% Ni powder) in a ball-mill. Binder is added to the $TaSi_2$ powder in 15 gram batches and the wafers are pressed at a load of 10,000 pounds and stored. Each wafer is one-half inch in diameter and weighs about 1.5 grams. Presintering is performed in vacuum at $1000^{o}F$ in 16 wafers batches. The final sintering is then carried out three wafers at a time. The wafers are heated up in vacuum to $1600^{o}C$ over a period of 5 minutes, held at temperature for 10 minutes and slowly cooled over a period of 10 minutes. About 100 wafers have been fabricated. They are all above 95% of theoretical density, and the majority are free of cracks.

Only the finishing of the wafer surfaces is not operating at full-scale. After many trials, a sequence of diamond discs for grinding, diamond pastes for lapping and a final polish of γ- alumina has been developed. The hardness of the silicides requires these techniques. Production of polished parallel surfaces on the $TaSi_2$ wafers has been a long and tedious operation.

In the first trial run, the diffusion pile consisted of $Ta/TaSi_2/Cb/TaSi_2/Ti/TaSi_2/Cr/TaSi_2/Ta$. This pile was run at $1900^{o}F$ (near the center of the desired experimental temperature range) for 4 hours. The main purpose of this run was to determine whether the molybdenum clamp would induce bonding between wafers. Therefore, no great pains were taken to produce perfectly finished surfaces. The only bonding that took place, however, was between the titanium and $TaSi_2$. This is understandable, since Ti is the lowest melting of the couple metals and deforms most readily at the test temperature.

The resulting increased contact area promotes bonding. In addition, the diffusion rate of the titanium may be higher than that of the other metals.

There appears to be no doubt that the molybdenum clamp does indeed exert pressure as a result of its small coefficient of expansion.

The second run again used Ta, Cb, Ti and Cr but included extra titanium and chromium wafers to act as pusher slugs by virtue of their high coefficient of expansion. This was done in order to observe the effect of increased pressure on bonding. Surfaces were more carefully prepared, and some were etched. The assembly was run under the same conditions as in run #1. No improvement in boding was observed.

The next two runs used the same assembly with additional pusher shegs to increase the pressure. Heating times were increased and the test temperature was kept the same. Although no more bonding took place, diffusion zones were distinguishable between $TaSi_2$ and Ti and Cr wafers. The chromium wafers were found to be much too porous for use in these studies, and may be abandoned in favor of molybdenum because of the difficulty of purchasing chromium in dense form.

Another exploratory run was performed at a higher temperature to determine whether bonding was at all possible with $TaSi_2$. The assembly was tested at 2500^oF for 6 hours, using a pure vanadium wafer in place of chromium. This run was successful. Only the vanadium did not bond, probably because the wafer was only half the diameter of the other wafers, and was in poor contact with the silicide wafers from the start of the run. After mounting and polishing, diffusion zones were clearly observable. Even though the vanadium was not bonded to the silicides, portions of an intermediate layer could be seen attached to the vanadium wafer. Again the titanium showed the thickest interdiffusion zone.

Future trial runs will work down from 2500°F to the lowest temperature at which bonding will take place. If a practical temperature range exists, data runs will begin. Otherwise a procedure of quick-bonding (raising the couple to a very high temperature for a very short time) will be employed to produce bonding with negligible diffusion before the test runs are made at the lower temperatures,

Program for the Next Six-Month Period

1. Thermochemical Data:

During the next six months the major effort will be directed toward completion of measurement on the electrodes formulated for the tantalum-silicon system. Initially, emphasis will be placed on those electrodes with low silicon content. Electrolyte material from each run will be examined by x-ray diffraction to determine if degradation has occurred. Silicide electrodes will also be examined by X-ray diffraction to determine the phases present before and after each run.

2. Glass Structure and Growth:

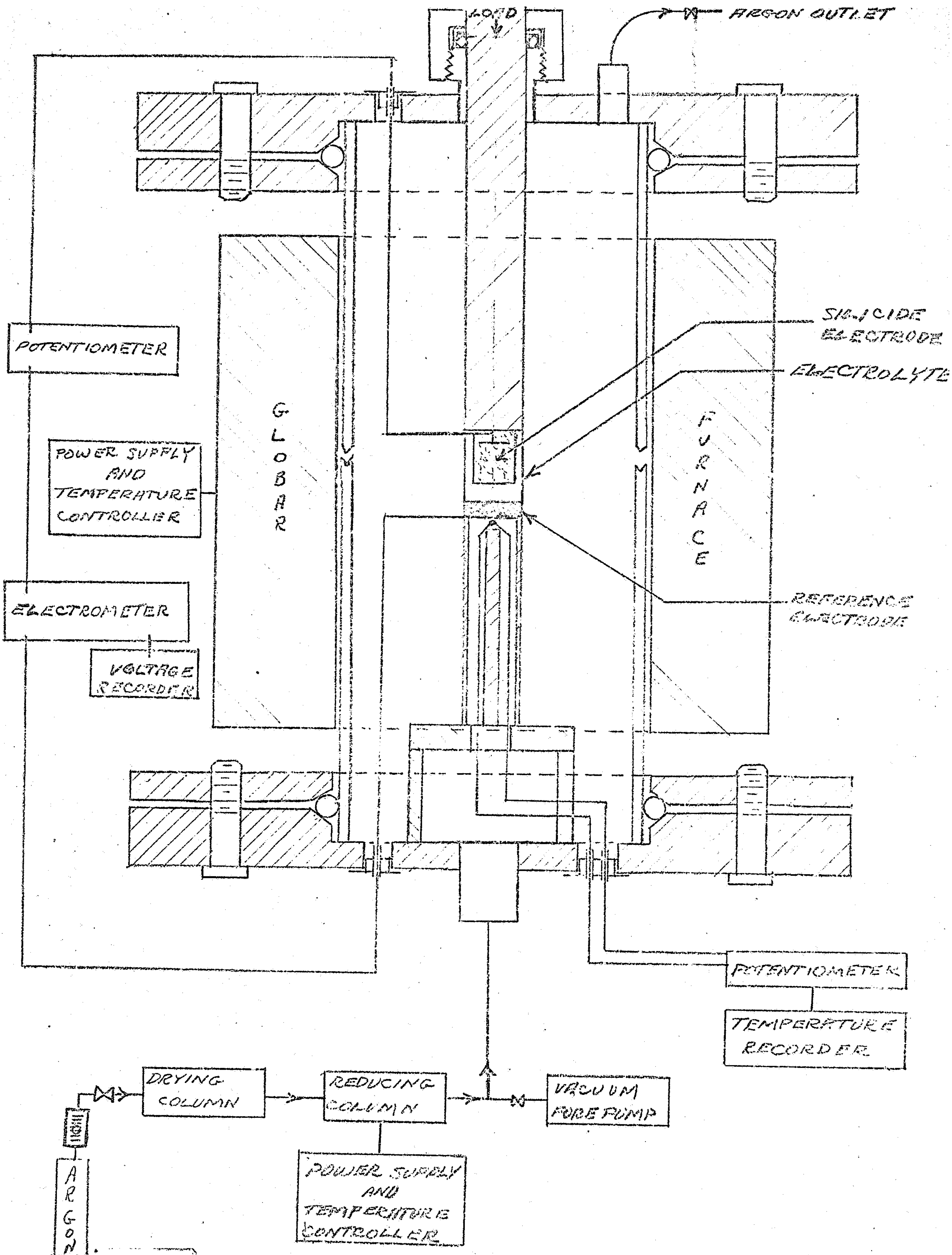
The oxidation of pure $TiSi_2$ in an oxygen-argon atmosphere will be studied in detail. The effect of temperature, time, oxygen pressure, sample density and surface preparation on the character and growth rate of the oxide film will be determined. The film will be followed by weight change, metallographic examination, x-ray and infra-red examinations. Electron microprobe analyses may be performed upon crucial samples

3. Oxidation Rates and Coating Modifiers:

Equipment for preparing experimental glasses will be constructed. The composition range for glass formation in the tantala-silica system will be explored. The influence of Al^{3+} - Ta^{5+} and B^{3+} - Ta^{5+} modifiers in improving glass-forming ability will be tested.

4. Substrate-Coating Interaction and Barriers;

It has now been established that adequate bonding for the diffusion studies is obtained between $TaSi_2$ and Cb,Ti,Cr,and Ta at 2500°F. The next series of experiments will establish a lower temperature limit for bonding, If this temperature is not sufficiently low, a bonding procedure employing high temperatures for short periods will be investigated. Data runs will then be made. Candidate materials for use as diffusion markers will be evaluated.


LOAD
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REFERENCE ELECTRODE
POTENTIOMETER
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GLOBAR
FURNACE
ELECTROMETER
VOLTAGE RECORDER
POTENTIOMETER
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DRYING COLUMN
REDUCING COLUMN
VACUUM FORE PUMP
ARGON
POWER SUPPLY AND TEMPERATURE CONTROLLER

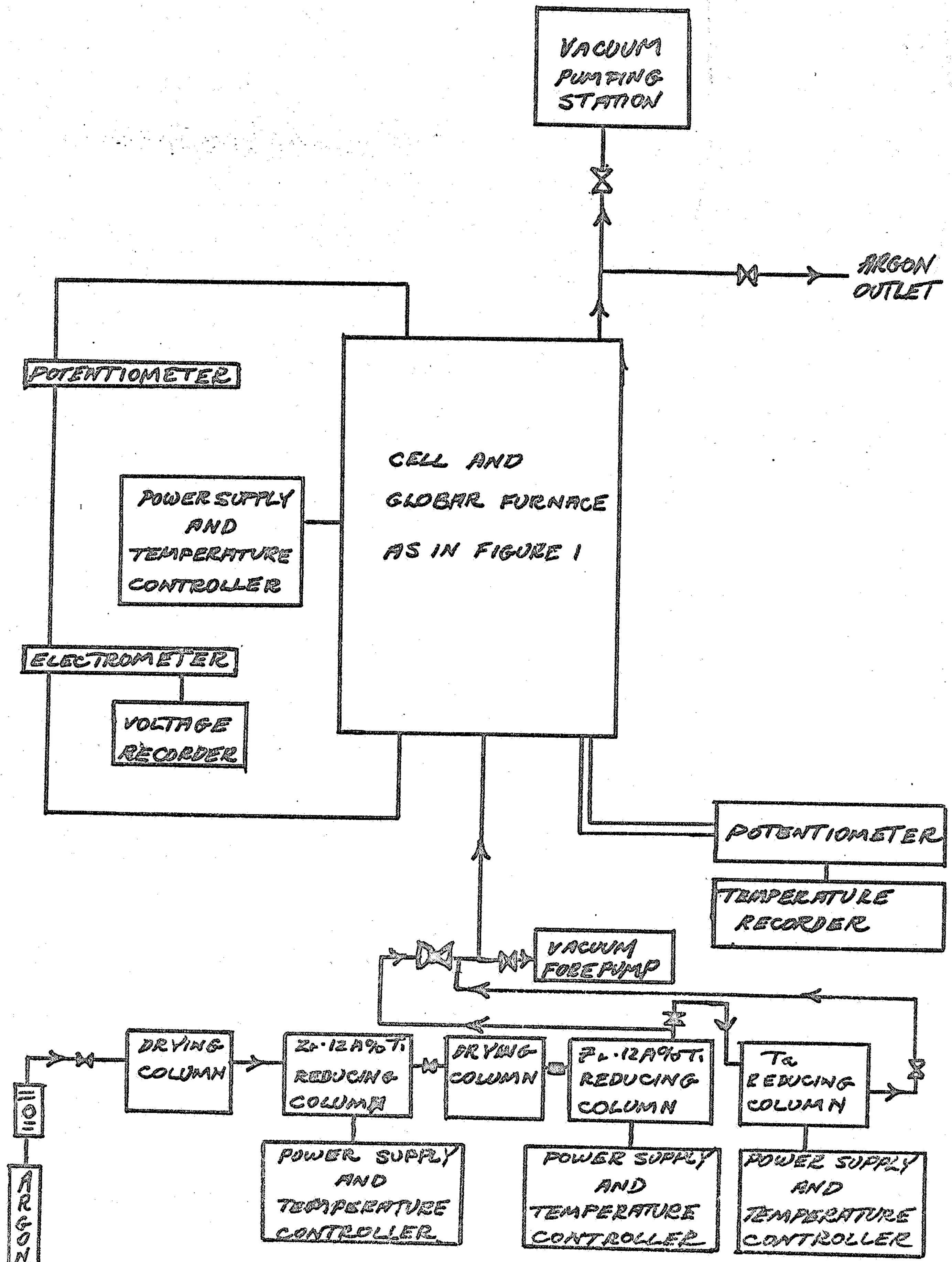

FIGURE 2. APPARATUS FOR EMF MEASUREMENTS

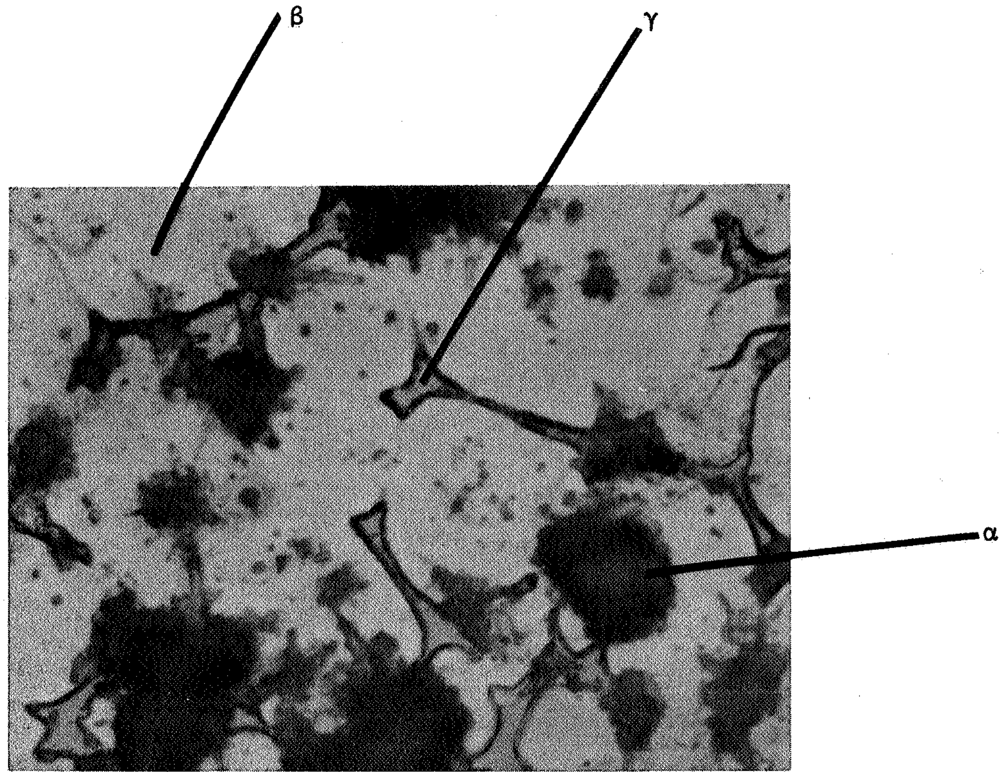

Figure 3. Oxide film on $TiSi_2$ after oxidation at 1900°F for 84 hours. Magnification 320X.

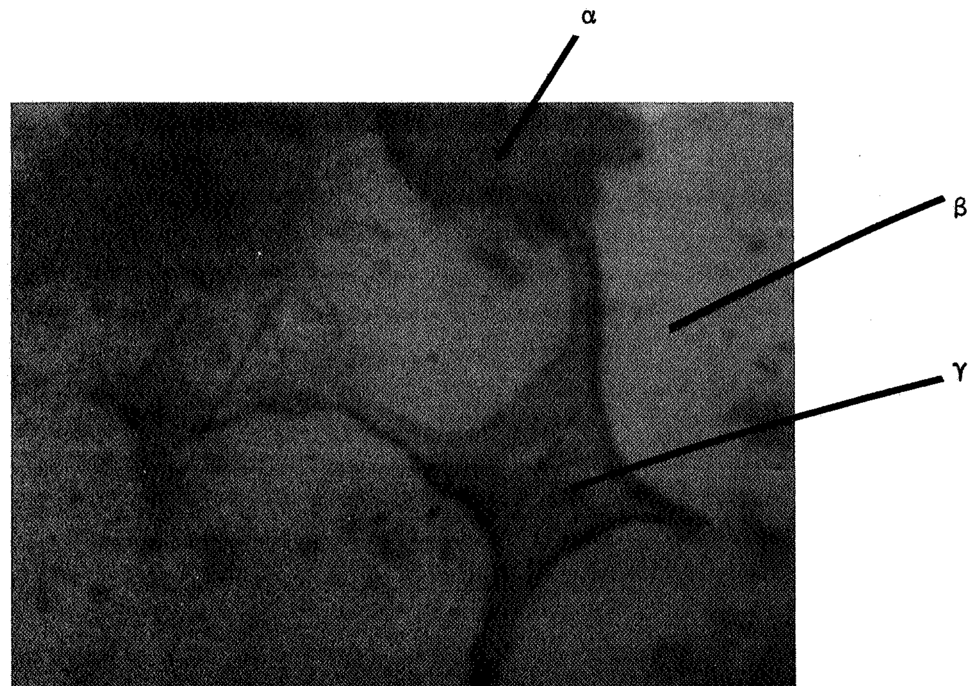

Figure 4. Oxide film on $TiSi_2$ after oxidation at 1900°F for 84 hours. Magnification 630X.

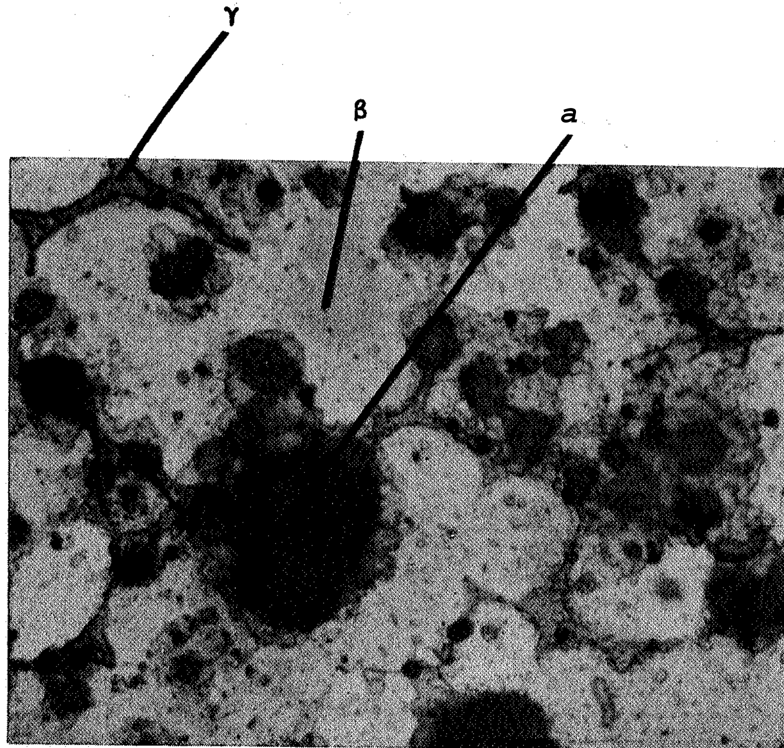

Figure 5. Oxide film on $TiSi_2$ after oxidation at 1500°F for 67 hours. Magnification 320X.

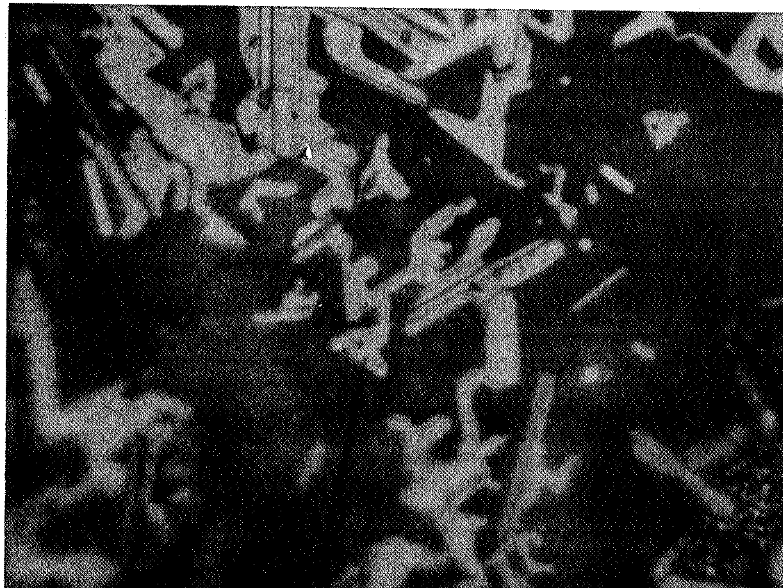

Figure 6. Oxide film on $TiSi_2$ after oxidation at 2400°F for 83 hours. Magnification 320X.

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