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N69-11038

FUNDAMENTALS OF THE OXIDATION PROTECTION OF COLUMBIUM AND TANTALUM

M. Kolodney, et al

New York University
New York, New York

1 October 1968

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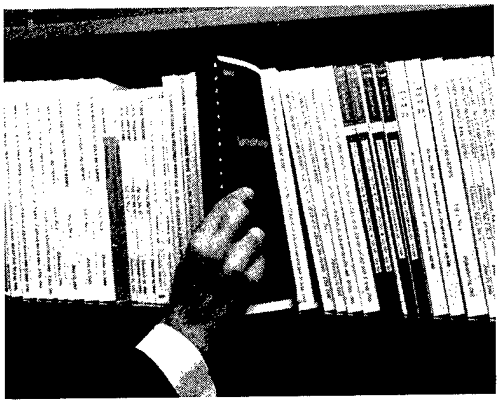

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THE CITY COLLEGE RESEARCH FOUNDATION
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NEW YORK, NEW YORK 10031

by

M. Kolodney and R.A. Graff

Prepared For

National Aeronautics and Space Administration
Grant NGR 33-013-017

October 1, 1968

FACILITY FORM 602

N69-11038	
(ACCESSION NUMBER)	(THRU)
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(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

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THE CITY COLLEGE RESEARCH FOUNDATION
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Semiannual Report No. 6
April 1, 1968 to October 1, 1968

FUNDAMENTALS OF THE OXIDATION PROTECTION OF COLUMBIUM AND TANTALUM

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Foreword

This is the sixth semiannual report on NASA Grant No. NGR 33-013-017. It covers work from April 1, 1968 to October 1, 1968.

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. The fourth report was issued October 1, 1967 and the fifth report on April 1, 1968.

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. George Halbfinger, Mr. Stanley R. Levine, Mr. Leon Schwartz and Mr. Frederic N. Schwettmann who are graduate students at The City College of New York. Mr. Andrew G. Mueller, a graduate student previously working on this project, has left college to enter the U.S. Army. Mr. Levine is presently preparing his dissertation. His work on thermochemical data will be continued by Mr. Halbfinger.

Start

Summary

An investigation of the fundamental processes involved in the protection of tantalum and columbium by their silicides all is in progress. The program has three 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. 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 program along with the efficacy of diffusion barriers to retard intermediate phase growth.

The previous reports described the development of specimen fabrication techniques, the design and construction of equipment and preliminary tests of some of the methods to be used. The free energies of formation all ~~formulation~~ of the tantalum silicides have been determined and are reported here. Fabrication of $TiSi_2$ specimens has been improved and new oxidation rates determined. Oxide films have been examined by infra-red spectroscopy, X-ray diffraction and electron microscopy. Growth rates of intermediate phases in a number of diffusion couples have been measured and are reported.

end

Contents

Introduction

Refractory metals are required for a variety of applications at elevated temperatures, particularly for air-breathing 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 reviewed 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-silicide and columbium-silicon systems, at temperatures up to 2500°F and under oxygen pressures of one atmosphere and above are under study.

Three major lines of investigation are in progress:

1) thermochemical data,
2) glass structure and growth,
3) 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 have been 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.

In the third 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, 1955), by Knudsen effusion (Myers and Searcy, 1957), or by reaction equilibria (Brewer and Krikorian, 1956). The average accuracy of the best available data is about ±15%. Much of the data is very poor. 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 have been determined from EMF measurements on electrochemical cells of the form:

$$\mathrm{Pt/Fe,Fe_xO//oxide\ electrolyte//silicide\ electrode/Pt}$$

where the free energy of the reaction is given by

$$\Delta G_R = -nFE$$

and ΔG_R contains the known free energies of formation of silica or β - Ta_2O_5 and Fe,Fe_xO 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.

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

The reference electrode half-cell reaction was

$$2\,e^- + Fe_xO \rightarrow Fe_x + O^=$$

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

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

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

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

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

Background material on solid oxide electrolytes has previously been presented (Kolodney and Graff, 1967 b, 1968).

EMF measurements on tantalum silicide electrodes were concluded during the past six month period. Successful runs on electrodes from each of the phase fields were made and free energies of formation of the tantalum silicides calculated.

The data for the successful runs are summarized in Table I. The first column lists the composition of the electrode as calculated from the starting materials. In the second column the sintering treatment is presented. The third column lists X-ray data which are indicative of the composition of the electrode after it was used in the cell. The ratios indicated are based on the intensity of the strongest X-ray diffraction peak for each of the compounds. The positions of the strongest peaks for each of the compounds are as follows: $TaSi_2$, d = 3.50; t-Ta_5Si_3, d = 2.34; Ta_2Si, d = 2.41; and $Ta_{4.5}Si$, d = 2.47. The fourth column lists the electrolytes used, their composition, sintering treatment and their density expressed as per cent of theoretical density.

Data for electrodes 1 and 2 were assigned to the electrode reaction expected for the Ta_5Si_3, $TaSi_2$ phase field:

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

Data for electrodes 3 and 4 were assigned to the electrode reactions expected for the Ta_5Si_3, Ta_2Si phase field. The assignments were made from X-ray examination of the electrodes before and after use

Table I

EMF Data for Silicide Electrodes with ThO_2-Y_2O_3 Electrolytes and an Fe,Fe_xO Reference Electrode

Silicide Electrode Composition	Sintering	X-ray Data	Electrolyte	Temp °C	EMF (mv)	Number of Observations
1) 74 wt % $TaSi_2$ 23 wt % Ta_5Si_3 3 wt % SiO_2 0.7 wt % Ni	1600°C, 15 min.	$\frac{I(TaSi_2)}{I(TaSi_2)+I(Ta_5Si_3)} = 0.50$	0.99 ThO_2 - 0.01 Y_2O_3 2000°C, 3 hrs ρ = 92%	900 1000 ±5	472 ±20 658 ±40	3 4
2) 74 wt % $TaSi_2$ 23 wt % Ta_5Si_3 3 wt % SiO_2 0.7 wt % Ni	1600°C, 15 min.	$\frac{I(TaSi_2)}{I(TaSi_2)+I(Ta_5Si_3)} = 0.83$	0.99 ThO_2- 0.01 Y_2O_3 2000°C, 3 hrs ρ = 94%	1000 1050 ±5 1100	560 648 692	1 2 1
3) 58 wt % Ta_5Si_3 38 wt % Ta_2Si 3 wt % TaO_5 1 wt % Ni	1620°C, 10 min.	$\frac{I(Ta_5Si_3)}{I(Ta_5Si_3)+I(Ta_2Si)} = 0.29$	0.93 ThO_2- 0.07 Y_2O_3 2000°C, 3 hrs ρ = 87.3%	1000 1050 ±5 1000	523 ±3 521 ±1 520 ±3	1 2 1
4) 56 wt % Ta_5Si_3 36 wt % Ta_2Si 7 wt % Ta_2O_5 1 wt % Ni	1620°C, 10 min.	$\frac{I(Ta_5Si_3)}{I(Ta_5Si_3)+I(Ta_2Si)} = 0.18$	0.93 ThO_2- 0.07 Y_2O_3 2000°C, 3 hrs ρ = 89.8%	800 850 900 ±5 950 1000 1045	537 ±4 565 ±4 578 ±8 583 ±4 589 ±9 585 ±4	1 2 5 4 6 2

Table I (concluded)

Silicide Electrode Composition	Sintering	X-ray Data	Electrolyte	Temp °C	EMF (mv)	Number of Observations
5) 42.2 wt % Ta_2Si 55.3 wt % $Ta_{4.5}Si$ 1.7 wt % Ta_2O_5 0.8 wt % Ni	1625°C, 15 min.	$\frac{I(Ta_2Si)}{I(Ta_2Si)+I(Ta_{4.5}Si)} = 0.39$	0.93 ThO_2- 0.07 Y_2O_3 2000°C, 3 hrs $\rho = 88\%$	900	556	2
				950	559	3
				1000 ±5	559 ±3	3
				1050	557	3
				1100	555	2
6) 42.2 wt % Ta_2Si 55.3 wt % $Ta_{4.5}Si$ 1.7 wt % Ta_2O_5 0.8 wt % Ni	1625°C, 15 min.	$\frac{I(Ta_2Si)}{I(Ta_2Si)+I(Ta_{4.5}Si)} = 0.22$	0.93 ThO_2- 0.07 Y_2O_3 2000°C, 3 hrs $\rho = 89\%$	850	554	1
				900	567 ±2	4
				950 ±5	563 ±2	2
				1000	562 ±9	5
				1050	560 ±3	4
				1090	562 ±7	3

in the cell and from micrographic examination. X-ray diffraction analysis of electrode 3 revealed a decrease in Ta_2Si content and an increase in Ta_5Si_3 content as a result of the cell reaction. Therefore the data observed for this electrode were assigned to the following electrode reaction:

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

Electrode 4 sustained a decrease in Ta_5Si_3 content and an increase in Ta_2Si content as a result of the electrode reaction. The following electrode reaction was assigned:

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

Finally data for electrodes 5 and 6 were assigned to the reaction expected for the Ta_2Si, $Ta_{4.5}Si$ phase field:

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

The EMF data were corrected for electronic conduction. The corrections (about +1%) were determined from earlier work with Ta,Ta_2O_5 electrodes. The upper bounds on data for electrodes 1 and 2 were adjusted to make them thermodynamically consistent. From the corrected data the free energies of formation of the tantalum silicides were computed. Free energy of formation data for the oxides of tantalum and silica were taken from Wicks and Block(1963) and free energy of formation data for wustite were taken from Charette and Flengas(1968). The results of the calculations are summarized in Table II. The data are thermodynamically consistent whereas earlier enthalpy of formation data were not.

Further details of this study may be found in a doctoral dissertation which is currently being written (Levine, 1968).

Table II

Free Energy of Formation of The Tantalum Silicides Per Gram-Atom of Silicon (kcal)

T°K	Δ G $TaSi_2$	ΔG Ta_5Si_3	ΔG Ta_2Si	ΔG $Ta_{4.5}Si$
1200		-24.8 ±3	-28.1 ±3.1	-38.5 ±7.2
1300	$-8.1\ {}^{+1.7}_{-3.7}$	-24.0 ±3	-27.2 ±3.1	-37.3 ±7.2
1400		-23.1 ±3	-26.1 ±3.1	-34.0 ±7.2

BCR/3.6

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 $TiSi_2$ may be considered.

Wafers of the silicides are prepared by the techniques of powder metallurgy. The initial oxidation studies were carried out in static air in a box-type furnace. Techniques for evaluating the character of the film were 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 may then be formulated.

Analytical Techniques

In earlier X-ray studies, the oxide film was removed from the $TiSi_2$ substrate using a chlorine etch at 700-800°C. The film was ground and a powder pattern obtained. The purchase of a Norelco diffractometer now allows the analysis to be made without destroying the sample. The oxidized specimen is placed in the sample support holder and the sample scanned. The resulting spectrum shows the $TiSi_2$ substrate quite strongly with smaller oxide peaks also present.

Both techniques will continue in use.

A more detailed analysis of the amorphous region of the oxide film is being carried out using infrared spectroscopy. A Perkin-Elmer Micro Specular Reflectance Accessory is being used on a Perkin-Elmer 621 Spectrophotometer. With this attachment radiation from the source is incident on the surface of the oxide film at an angle of 13°. The incident radiation is transmitted through the film, reflected off the substrate, passed back through the film and out to the detector. The spectrum thus normally obtained is a 2x absorption spectrum which can be compared with literature data on amorphous silica and glasses.

Electron microscopy is also being used to examine the surface structure of both the $TiSi_2$ and the growing oxide film. Initially, the sample is etched to reveal the microstructure. A film of nitrocellulose from a 4% collodion solution is then formed on the surface. The film is removed, shadowed with platinum which is then covered by a thin layer of carbon. The nitrocellulose is then dissolved in amyl acetate and the carbon replica dried. A Phillips model 300 Electron Microscope is being used in the analysis.

Sample Preparation

The $TiSi_2$ powder in this study was obtained from CERAC, Inc. and had a minimum purity of 99.6%. Metallographic examination of the polished wafers made from this material showed a second phase at the $TiSi_2$ grain boundaries. The majority of the holes in the sample surface are found in this phase believed to be silicon. In order to obtain better surfaces, two methods for obtaining better purity powder are being studied.

One method consists of reacting high purity titanium and silicon with only a slight excess of silicon (0.1%) at 1000°C. The partially sintered reaction product is then ground and the -400 mesh material collected. The wafers are then fabricated in the usual way.

Metallographic and X-ray analysis indicate only $TiSi_2$, with no silicon. In addition the surface has considerably fewer holes.

The second method involves reacting the CERAC $TiSi_2$ with 10% NaOH at 50°C for 2 minutes. The silicon is dissolved in the caustic while the $TiSi_2$ is not. The $TiSi_2$ is washed with water, dried, ground and the -400 mesh material removed. This powder gives surfaces similar to those obtained by judicious direct reaction of the elements.

Oxidation Studies

A 100 hour oxidation run has been completed using a sample prepared by direct reaction of the elements. The oxidation was carried out at 1000°C with an oxygen partial pressure of 0.2. The oxide film that was formed appeared to be structurally similar to those obtained using the CERAC $TiSi_2$.

A significant difference was observed however in the rate of oxidation. Where in the earlier runs slopes of 3 to 4 were obtained when plotting the log of the weight gain against the log of time, the new sample gave a value of 2.07 for the slope. The weight gain was lower being only 50% greater than that obtained for the oxidation of silicon.

Character of the Oxide Film

300°C

At 300°C, where the weight gain is almost negligible, no visible oxide can be seen after oxidizing for 300 hours. A few, very small multicolored crystalline areas are observed on the sample surface when viewed at a magnification of 400X. X-ray analysis shows only the $TiSi_2$ substrate. Under polarized light the entire field is dark.

The infrared spectrum using 5X ordinate expansion shows a broad, low intensity absorption at 1250 cm^{-1}, a very faint absorption at 1020 cm^{-1}, a slight depression at 810 cm^{-1} and a moderately strong, broad peak at 650 cm^{-1}.

600°C

At 600°C after 200 hours oxidation, a multicolored, transparent oxide film is formed. In each area corresponding roughly in size and shape to the substrate grains, one of two or three colors is observed. Light microscope examination of the film reveals no crystalline growth areas. X-ray analysis indicates only the $TiSi_2$ substrate. Observation under polarized light shows lighter colored areas within the holes in the surface.

The infrared spectrum shows peaks at 1020, 800 and 650 cm^{-1}. A slight bump centered at 1200 cm^{-1} and a small peak at 940 cm^{-1} were also observed.

800°C

At 800°C a transparent oxide film is also formed. In this case crystalline TiO_2 (rutile) is observed to occur between 3 and 7 hours of oxidation. The TiO_2 is segregated in clumps about 50 microns in diameter.

The infrared spectrum shows definite absorptions at 1255, 1060 and 650 cm^{-1}. The peak height for the 1255 cm^{-1} absorption is greater than for the 1060 cm^{-1} although the 1060 cm^{-1} is broader. No absorption is observed at 800 cm^{-1}.

1000°C

At 1000°C, the oxide film is similar to that obtained at 800°C. X-ray and metallographic studies indicate an amorphous silica matrix with crystalline islands of TiO_2 (rutile). The crystallization occurs after about 1 hour at reaction temperature.

The infrared spectra of a number of samples were recorded during the course of their oxidation. For reaction times greater than 50 hours, the peak positions appear to be relatively stable. Strong absorptions are observed at 1254, 1065 and 780 cm^{-1}. During the course of oxidation the position of the 1250 cm^{-1} peak appears unchanged. The position at the 1065 cm^{-1} peak changed from 1000 to 1065 cm^{-1} as the oxidation time increases from 1 to 100 hours.

1200°C

The characteristic amorphous silica matrix with crystalline TiO_2 (rutile) is observed. Crystallization occurs within 0.5 hours at temperature. X-ray analysis also indicates that α-cristobalite is present at 0.5 hours. Microscopically, many small multicolored crystalline-like areas appear after about 50 hours. The TiO_2 islands appear to grow with time.

The infrared spectra of the oxide are quite different from those obtained at lower temperatures. The bands at 1240 and 1050cm^{-1} have each split into two bands. The major bands are located at 1240 and 1058 cm^{-1} with secondary bands at 1195 and 950 cm^{-1}. Each of the bands is considerably stronger and sharper than at the lower temperatures. In addition there are sharp bands at 785 and 465 cm^{-1}.

Discussion

When attempting to formulate a mechanism by which a material oxidizes, it is essential that the character and structure of the growing oxide film be known. In the oxidation of $TiSi_2$ in the region 300-1200°C, the oxide consists of an adherent, amorphous silica film. Above 700°C islands of crystalline TiO_2 (rutile) appear. Above 1100°C, α-cristobalite is also observed. In the entire region the oxide film is quite protective.

The nature of the amorphous region in the oxide film requires closer study. At the higher temperatures this region is fairly uniform in color. At lower temperatures, i.e. 600°C, the film is several colors, each color region corresponding in size and shape to the $TiSi_2$ grains. This is probably due to a difference in thickness caused by a variation in oxidation rate with substrate orientation.

Bulk amorphous SiO_2 shows absorption peaks at 1250, 1100, 800 and 460 cm^{-1}. The structural significance of the last three has been discussed by Lippincott et. al. (1958). He attributes the 1100 cm^{-1} vibration to Si-O stretching, the 800 cm^{-1} vibration to Si-Si stretching and the 460 cm^{-1} vibration to Si-O bond bending. No mention is made of the structural significance of the 1250 cm^{-1} peak.

In the present study the 1250 and 1100 cm^{-1} absorptions were present in all samples. The 1250 cm^{-1} peak was usually in the same position, while the 1100 cm^{-1} vibration was found at a consistantly lower value. This varied from 1020 cm^{-1} at 600°C to 1065 cm^{-1} at 1000°C. Position also varied with time of oxidation, starting at 1000 cm^{-1} at 1 hour to 1065 cm^{-1} at 100 hours. The 800 cm^{-1} vibration was also present in most samples although it was not a sharp peak but rather a bump in the baseline. The 460 cm^{-1} absorption was normally observed only at long times and high temperatures.

It is difficult at this time to say whether the shifting of bands to a lower frequency is due to a more disordered silica or to the entrapment of titania in the lattice. In addition the shift could also be due to a more porous oxide or a difference in oxide thickness. At 1200°C the band splitting could be caused by the partial crystallization of the amorphous SiO_2 to α-cristobalite or to a TiO_2-SiO_2 glass formation. The former explanation appears more reasonable at this time since no phase separation, which would be expected for a SiO_2-TiO_2 glass, is observed using electron microscopy.

Concerning the mechanism by which the film forms, the latest 1000°C run showing parabolic behavior would appear to indicate diffusion control. The appreciable dependency of reaction rate on crystal orientation at 600°C would tend to indicate a surface reaction controlling mechanism. The earlier cubic and quatric results appear to be due to the holes present in the sample surface. A slowly decreasing area during the course of oxidation could give rise to a higher order.

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, presumbly 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.

In the method used here, wafers of the substrate metal and coating material are contacted under pressure at the temperatures of interest. Rates of growth of the intermediate silicides are measured. The same techniques are applied to measure and explain the performance of additive or barrier elements such as titanium. Preliminary runs were described in the previous report (Kolodney and Graff, 1968).

The results of the analysis of the first twelve diffusion runs (just about one-half of the experimental schedule) are plotted in Fig. 1. The line for $Ta/TaSi_2$ couples was obtained by least squares analysis of 12 data points and is described by the parabolic growth constant K

$$K = 26\ e^{-80,000/RT}$$

where the activation energy Q is known with 95% certainty to lie between 70 and 90 Kcal/mole. This can be compared to Bartlett's (1966) result which, in the same form, yield:

$$K = 35\ e^{-58,000/RT}.$$

The remaining lines were drawn visually, since there were not enough data to warrant a least squares analysis. Those points listed as missing data represent couples that have been run, but in which the bonding was so poor (or ruined in preparation for microscopic examination) that no useful data could be recorded. Eight Re/$TaSi_2$ couples were run, but only one data point could be recorded, and since that one is in doubt, results of Re coupling with $TaSi_2$ have been omitted.

Two observations may be noted from these graphs: First, the growth rate of the intermediate in the Mo/$TaSi_2$ couple is unusually high. Second, a strange break occurs in the Mo and W plots at 2300° and 2400°F respectively. This is quite possibly due to poor contact below the break temperatures since the diffusion zones at the lower temperatures in these couples are extremely porous. None the less, the fact that only these materials exhibit discontinous behavior suggests that this is a result of the particular metal silicide properties.

The clearest conclusion to be reached from the results presented is the need for more data. It is expected that the remaining diffusion couples will clarify the trends, and confirm any unusual behavior.

The delay in completing the experimental schedule is the result of difficulties encountered in producing dense $TaSi_2$ wafer specimens. The techniques which had previously reproducibly yielded dense $TaSi_2$ wafers failed to produce acceptable results when sample production was resumed in April. Since that time much effort has been expended in trying to sinter $TaSi_2$ that would be usable in the diffusion experiments. Examination of many specimens leads to the assumption that the amount of Ta_5Si_3 present in the $TaSi_2$ is critical in producing relatively "hole-free" $TaSi_2$ wafers. In fact, the only batch to yield satisfactory $TaSi_2$ in the past 5 months had a high concentration of Ta_5Si_3. Some of these wafers have been used in diffusion couples and the effect of initial Ta_5Si_3 concentration in the $TaSi_2$ on diffusion will be analyzed.

Six more diffusion runs have been made utilizing these $TaSi_2$ (high Ta_5Si_3) wafers, leaving only seven runs to complete the experimental schedule.

X-ray analysis across the diffusion couple is now in progress. X-ray data for a rhenium silicide (probably Re_5Si_3) hitherto unrecorded has been observed and will be confirmed. Diffusion data are being plotted as zone-thickness profiles and will be analyzed together with the X-ray data to ascertain the nature of the intermediate phases in the $M/TaSi_2$ couples.

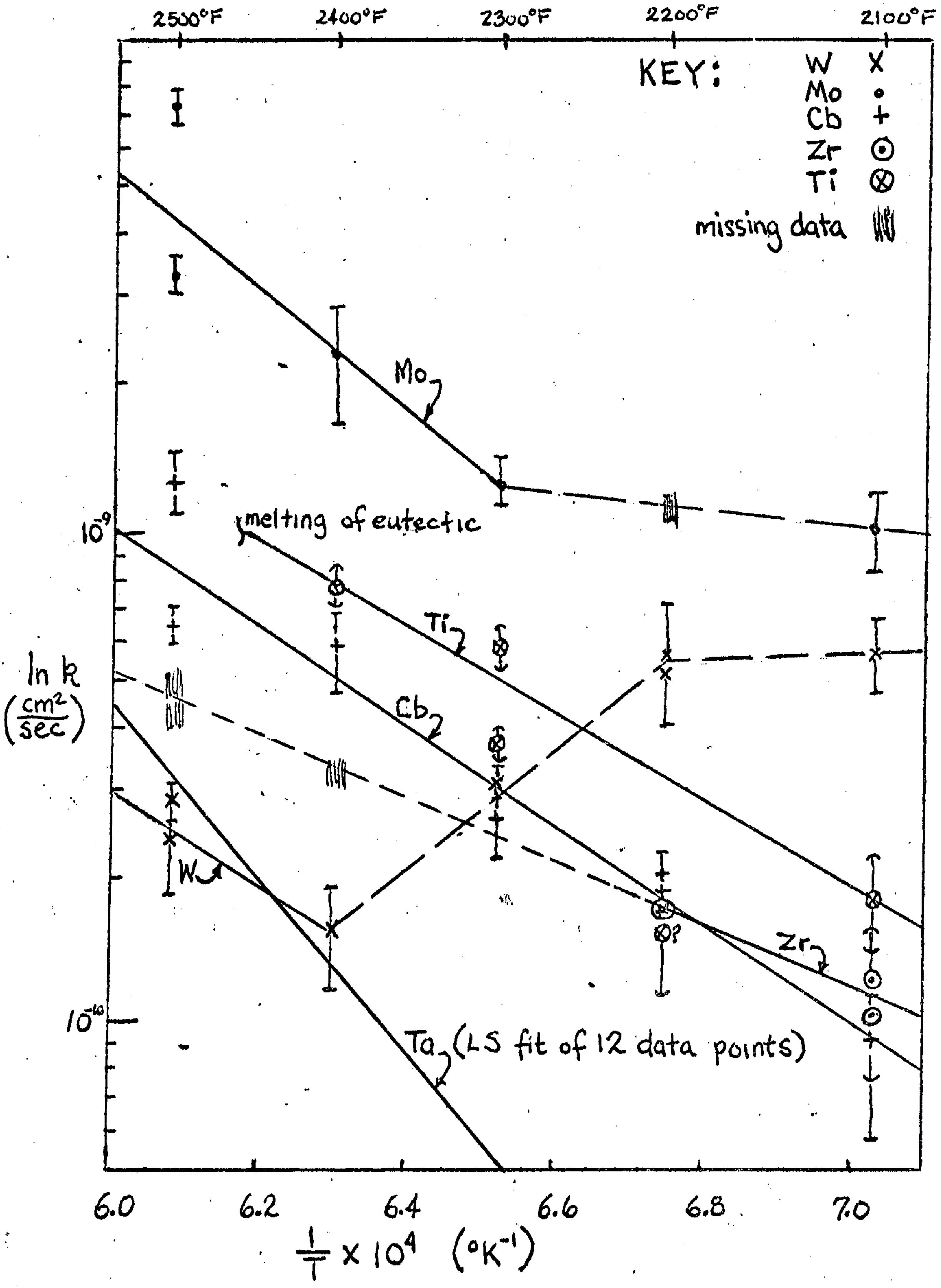

Fig. 1. Parabolic Growth Constants for Intermediate Silicides

Program for Next Six-Month Period

1. Thermochemical Data: The electrolytic cell will be redesigned to reduce the leakage of oxygen from one electrode to the other. This should substantially improve the reliability of the e.m.f. measurements on tantalum silicides.

2. Glass Structure and Growth: In order to confirm the latest parabolic result, additional samples, prepared either by caustic washing or direct reaction of the elements, will be oxidized. In addition TiO_2-SiO_2 glasses will be prepared to help clarify the infrared results. An attempt will also be made to determine the refractive index of the oxide film using an immersion technique.

3. Substrate-Coating Interaction and Barriers: Additional diffusion couples will be annealed, and X-ray analyses of the intermediate phases will be continued. Profiles of the intermediate zones will be plotted and interpreted.

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