THE CITY COLLEGE RESEARCH FOUNDATION
THE CITY COLLEGE, THE CITY UNIVERSITY OF NEW YORK
NEW YORK, NEW YORK 10031

Semiannual Report No. 8
April 1, 1969 to October 1, 1969

FUNDAMENTALS OF THE OXIDATION PROTECTION OF COLUMBIUM AND TANTALUM

By
M. Kolodney and R.A. Graff

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

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Foreword

This is the eighth semiannual report on NASA Grant No. NGR 33-013-017. It covers work from April 1, 1969, to October 1, 1969.

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. Additional reports were issued October 1, 1967, April 1, 1968, October 1, 1968 and April 1, 1969.

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. Leon Schwartz and Mr. Frederic N. Schwettmann who are graduate students at The City College of New York. Mr. Stanley R. Levine, a graduate student previously working on this project has completed his research. His work on thermochemical data has very recently been published. It is being continued by Mr. Halbfinger.

Summary

An investigation of the fundamental processes involved in the protection of tantalum and columbium by their silicides is in progress. The program has three parts. The first part was devoted to establishing thermochemical data for the silicides and employed 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, preliminary tests, and a number of results. The free energies of formation of the tantalum silicides have been determined and reported and are summarized here. Methods for improving the solid state electro-chemical cell are now being investigated.

In order to understand the characteristics of glass formation, the oxidation behavior of titanium disilicide has been studied and compared with the known behavior of molybdenum disilicide and tantalum disilicide. It has been found that unlike pure $TaSi_2$, $TiSi_2$ displays excellent oxidation resistance. Furthermore, unlike $MoSi_2$, titanium disilicide shows no "pesting" at any temperature from about 300°C (572°F) to above 1200°C (2200°F). This good performance is attributed to the partial solubility of titanium atoms in the silica lattice and the relatively rapid segregation of TiO_2 without interfering with the formation of sound SiO_2 glasses.

The study of the growth of intermediate phases in the system composed of $TaSi_2$-Ta has been nearly completed. The growth of the Ta_5Si_3 layer has been measured with good precision. It has been found that it represents a very significant mode of degradation of tantalum disilicide and that at temperatures approaching 2500°F, thick coatings would be needed to permit lifetimes of a few thousand hours. Barriers of tungsten, columbium, zirconium, titanium and molybdenum have been investigated. They have been found less effective than tantalum.

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. At temperatures proposed for their use, oxidation rates are prohibitive, and a protective coating is required. Silicide and aluminide coatings have been most successful.

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-silicon system, at temperatures up to 2500^{o}F and under oxygen pressures of one atmosphere and less are being investigated.

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. The free energies of formation of the silicides of tantalum have been determined in the first part of the program using a solid galvanic cell at elevated temperature.

The oxidation protection by silicides depends upon the formation of a glassy silica film which acts as a barrier to oxygen. Molybdenum disilicide is known to possess excellent oxidation resistance at high temperatures, but at lower, temperatures the coating fails. This behavior is presumed to be associated with the volatility of its oxide, MoO_3, at high temperatures, whereas at lower temperatures it is retained in the silica and prevents formation of a satisfactory glass. By this reasoning, $TaSi_2$ is not protective because its oxides Ta_2O_5 is not volatile at high temperatures. It might then be expected that any metal which forms a very stable, non-volatile oxide should be incapable of forming protective silicides. However, it is known that titanium modifiers to tantalum silicide coatings appear to improve the oxidation resistance. Yet TiO_2 is not volatile and is thermodynamically more stable then Ta_2O_5. A study of the oxidation behavior of pure TiO_2 was undertaken in order to explain this apparent anomaly.

In addition to degradation by oxidation, a disilicide coating may fail because of the loss of silicon to the substrate by diffusion. The resulting intermediate phase (Ta_5Si_3 in the $TaSi_2$-Ta system) is not resistant to oxidation. Hence, the rate of loss of coating by this mechanism may limit its life. In order to study the diffusion process over substantial periods of time, thin coatings are not adequate and massive wafers are needed. These wafers also allow investigation of the interaction of $TaSi_2$ with metals other than tantalum. Such metals may possibly be employed as barriers to the loss of silicon from tantalum disilicide.

Thermochemical Data

The free energies of formation of the tantalum silicides have been determined from EMF measurements on cells with solid thoria-yttria electrolytes. Measurements were conducted in the temperature range 900°-1100°C in a purified argon atmosphere. Corrections for electronic conduction, established with Ta, Ta_2O_5 electrodes, were applied to the measured voltages. At 1300°K (1880°F) the standard free energies of formation in kcal per gram atom of silicon were found to be:

$TaSi_2$ -8.1 (+1.8, -3.7), Ta_5Si_3 -24.0 ($\pm$3), Ta_2Si -27.2 ($\pm$3.1), $Ta_{4.5}Si$ -37.3 ($\pm$7.2). These results were presented in Semiannual report No. 6 and the details of the experimental work have been published in the October 1969 issue of the Journal of the Electrochemical Society 116, 1420 (1969). The results have proven of value in qualitative predictions of barrier interactions.

The major difficulties encountered in the method resulted from the hard, refractory nature of the silicide - based electrodes which prevented fabrication of dense electrodes. Work is now in progress to improve the reliability of high temperature measurements by obviating the need for dense electrodes. This work has been deviated to a study of fabrication techniques for electrolytes and the manufacture of cermet electrodes. It has not yet progressed to the stage of producing significant data.

Glass Structure and Growth

The experimental work for this portion of the study has been completed and a thesis has been written. The details of the investigation and the results are being compiled for publication.

Wafers of the silicides were prepared by the techniques of powder metallurgy. Oxidations were performed in a tube furnace with controlled atmosphere. Analytical techniques were developed for determining the character of the oxide film. These include X-ray diffraction, infrared spectroscopy, and electron microscopy. The results of the oxidation experiments have been given in the last two reports along with a description of the character of the films formed at temperatures between 300° and 1200°C, but the significant results will be summarized here prior to later detailed publication.

Methods were developed for the synthesis of titanium disilicide and for the fabrication of substantial wafers in dense form and with excellent surfaces. These were oxidized in argon-oxygen atmospheres at controlled temperatures in the range of 300°C to 1200°C (572°F - 2192°F). Weight changes were followed by means of a microbalance.

It was found that titanium disilicide possessed excellent oxidation resistance over the entire range studied. Its ability to resist oxidation is not greatly inferior to that of pure silicon. There was no indication of "pesting" at any temperature. At low temperatures, any TiO_2 formed appeared to be retained in the silica glass, but at higher temperatures, segregated islands of TiO_2 with the structure of rutile were formed. Nevertheless, the glass was stable, amorphous and resistant to the entry of oxygen. Hence, it appears to be conclusively proven that it is possible to obtain good protective silicide coatings on metals whose oxides are both more stable than SiO_2 and are also not volatile. This conclusion is in direct contradiction of the earlier inferences based upon the

oxidation behavior of $MoSi_2$ and pure $TaSi_2$.

The favorable performance of $TiSi_2$ may account for the value of titanium additions to tantalum disilicide coatings. (Diffusion studies in the Substrate - Coating Interaction portion of the program have shown that titanium is of no value as a barrier to silicon diffusion.) Its performance is attributed to the partial solubility of titania in silica and perhaps to the ease of segregation after the solubility has been exceeded. It has been shown that the TiO_2 islands appear to exist above a layer of silica glass rather than penetrating directly to the disilicide surface.

A brief study was made of lower titanium silicides. It was found that although protective, they were not as effective as $TiSi_2$. In addition, it was shown that a mixture of $TaSi_2$ - $TiSi_2$ was superior to $TaSi_2$ alone.

The details of the experimental results are being compiled for publication, but the parabolic growth constants at 1000°C are given in Table I.

Table I

Parabolic Rate Constants At 1000°C For Materials In The Titanium-Silicon System

Material	K, $(m_g/cm^2)^2/hr$	
Silicon	1.57×10^{-4}	(a)
$TiSi_2$	3.52×10^{-4}	
TiSi	90×10^{-4}	
Ti_5Si_3	0.65	
Titanium	3.6	(b)

(a) Deal and Grove (1965)

(b) Kofstad (1966)

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 coating life.

In the method used here, wafers of the substrate metal and coating material were contacted under pressure at the temperatures of interest. Rates of growth of the intermediate silicides were measured. The same techniques were applied to measure and explain the performance of additive or barrier elements such as titanium, tungsten, columbium, molybdenum and zirconium.

The experimental work has been essentially completed and a detailed report in the form of a thesis is being written. The rate of growth of the intermediate diffusion layer on the tantalum disilcide - tantalum system has been measured with good precision. The growth of layers between $TaSi_2$ and the other possible barriers has been measured with lower precision, but well enough to define their barrier characteristics. In addition, the nature of the intermediate phases has been investigated and they have been identified in most cases.

Summarized briefly, it has been found that the growth rate of Ta_5Si_3 is given by the following expression:

$$K = 5 \exp(-77{,}000/RT)$$

Where K is the parabolic growth constant in the equation

$$x^2 = Kt$$

with x being the thickness of the intermediate layer in cm. and t is the time in seconds. The value of the activation energy is known

with 95% confidence to be between 74,000 and 80,000 calories/mole and the pre-exponential constant is known with the same confidence to be between 2 and 11 cm^2/sec.

The results of this study are in substantial disagreement with those of Bartlett (1966), whose equivalent constant would be

$$K = 36.6 \exp(-58,000/RT)$$

There also appears to be a very large discrepancy between Bartlett's graphical data and his pre-exponential constant. It should be noted that Bartlett employed coated samples whereas wafers were used in the present study. The use of wafers permitted longer diffusion anneals.

The rate of degradation of $TaSi_2$ was measured separately. This should be identical with the rate of growth of $TaSi_3$ on the $TaSi_2$ side of the original interface. In terms of its parabolic growth constant, it was found to be

$$K_1 = 2 \exp(-81,000/RT)$$

The practical significance of these results may be expressed in the form of Table II. Inspection of these

Table II

Calculated Time To Grow A 1 Mil Layer of Ta_5Si_3 And Lose 1 Mil of $TaSi_2$ (for layers other than 1 mil, multiply time by square of layer thickness in mils.)

	Time (Hours)		
	1500°F	2000°F	2500°F
To grow 1 mil Ta_5Si_3	10^6	600	5.3
Life of 1 mil $TaSi_2$			
as measured directly	1.4×10^7	6600	45
as calculated from K	0.7×10^7	4200	37

data indicates that at temperatures above 2000°F, the lifetimes of silicide coatings on tantalum may be limited by diffusion onto the substrate rather than by oxidation phenomena. As the operating temperature approaches 2500°F, a coating thickness of about 10 mils may be needed for a life of several thousand hours.

The wafer technique also permitted an evaluation of the feasibility of using barrier metals to limit the interaction of the coating with the substrate. While the detailed results have not been fully compiled, it has been found that none of the barriers tested (tungsten, columbium, zirconium, titanium and molybdenum) may be regarded as successful. All were no better than tantalum, or were poorer. In order of decreasing effectiveness they are:

tungsten
columbium and zirconium
titanium and molybdenum

The details of the intermediate phases formed when using barrier metals in contact with $TaSi_2$ are being compiled and will be reported later.

Program for Next Six-Month Period

1. Thermochemical Data: Work on improved methods of equilibration and fabrication of electrolytes has been started, and will be continued.

2. Glass Structure and Growth: The effect of oxygen on the solubility of TiO_2 in SiO_2 is being studied further. A full report of this phase of the program is being compiled for publication.

3. Substrate-Coating Interaction and Barriers:

   The results of the experimental work are being assembled in the form of a thesis and will be prepared for publication.

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