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MECHANISM OF THE OXIDATION OF
TITANIUM DISILICIDE: 300 - 1300°C

by

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1. Introduction

In recent years, there has been an increasing demand for structural materials which can be used at temperatures as high as 2400°F (1316°C). One such application is in the turbine components of the proposed supersonic transport. At present, the refractory metals, in particular tantalum and columbium (niobium) are being considered for this application because of their high strength at these temperatures (1,2). These materials, however, have a major drawback in that they oxidize very rapidly. They also suffer from hardening and embrittlement by oxygen and nitrogen absorption. Attempts to improve the oxidation resistance of tantalum or columbium by alloying have met with only marginal success. At present, the most effective results are obtained by the use of protective coatings, in particular those of silicides and aluminides.

A silicide coating is normally formed by reaction of silicon with the preshaped metal. The coating, which is usually several mils thick, grows by diffusion of silicon through the silicide followed by reaction of the silicon with the metal at the coating-metal interface. The coating is chemically bonded to the substrate.

In order for the silicide coating to provide oxidation resistance, it is necessary that an adherent oxide film be formed when the material is exposed to an oxidizing atmosphere. The oxide film then acts as a barrier which limits further ingress of oxygen to the coating surface.

A simple coating of $TaSi_2$ formed on tantalum does not provide oxidation resistance (3). In order to obtain a suitable coating, it is necessary to add modifiers such as chromium, titanium, molybdenum and vanadium during the coating preparation (4,5). The final coating is a mixture of the various metal silicides. In some of the more

promising systems, the resulting protective layer consists mainly of TiSi_2 . The mechanism by which TiSi_2 enhances the oxidation resistance of the silicide mixture has not been determined. In addition, the intrinsic oxidation behavior of bulk TiSi_2 has not been studied.

Determination of the fundamental oxidation mechanism for a silicide when in the form of a coating is difficult because of physical defects in the coating and uncertainties in its chemical composition. Also, interactions between the coating and substrate can be a significant factor in long term oxidation resistance.

The purpose of this study is threefold:

1. Obtain data on the oxidation of bulk TiSi_2 in the temperature region 300-1300°C.
2. Develop a mechanism to describe the oxidation.
3. Relate this mechanism to results obtained with other silicides and determine whether a consistent theory of oxidation protection can be applied to this general class of materials.

11. Oxidation Theory

In a simple oxidation reaction, a metal and oxygen gas combine to form a metal oxide. At the start of the reaction, oxygen is adsorbed on the metal surface. As reaction occurs, an oxide layer forms, separating the reacting metal and gas. At this point, transport of one of the reacting species through the oxide is required in order for the reaction to continue. If the oxide is porous or spalls from the surface, transport is easy, while an adherent, dense oxide will help prevent further oxidation.

In determining a mechanism for a particular reaction, the usual practice is to find the step which is rate controlling. Assuming an initial oxide film is formed, the sequence of steps that are involved in order for reaction to occur are: transfer of oxygen through the gas to the oxide surface, adsorption on the oxide, diffusion of either or both of the reacting species through the oxide film and reaction at the appropriate interface. In most oxidation reactions, either a surface reaction or diffusion through the film is found to be the rate controlling step.

A considerable number of equations have been developed based on a particular rate controlling step. It is important to keep in mind that a fit of a particular equation by the data does not in itself determine the oxidation mechanism. Rather, it classifies the oxidation behavior and limits the interpretation to a group of mechanisms.

The most commonly encountered "laws" may be classified as linear, parabolic or logarithmic. These represent limiting and ideal cases. Deviations and intermediate rate expressions are frequently encountered and in many cases it is difficult to fit rate data to any of the simple models.

The simplest rate expression is derived from the case where reaction at an interface is the controlling step. This could include the adsorption of oxygen onto the surface or reaction to form the metal oxide at the metal/oxide interface. In this situation, there is no concentration gradient of the diffusing species across the oxide film. The reaction rate is then independent of the thickness of the oxide and, therefore, independent of time. This linear oxidation can be described by

$$X = k_1 t + c_1,$$

where X is either oxide thickness or weight gain, t the time, k_1 the linear rate constant and c_1 a constant of integration.

In many high temperature oxidations, the rate controlling step is the diffusion of oxygen or metal through the growing oxide film. This particular mechanism has been studied most extensively with a firm theoretical foundation being supplied by Wagner (6). His development shows that a parabolic expression of the general form

$$X^2 = k_p t + c_p$$

where k_p and c_p are constants, is obtained when species diffusion is rate controlling. The parabolic rate constant, k_p , is essentially a function of the species diffusivities and as such is dependent on the oxygen partial pressure and temperature.

The Wagner theory is based on transport through the film by a lattice diffusion mechanism. There are also cases where diffusion occurring along grain boundaries or other low resistance paths is an important if not predominant mode of transport. This is particularly true at low temperatures where bulk diffusion may be very small. As oxidation proceeds, it is generally assumed that the low resistance paths are eventually blocked by fresh oxide. Depending on the expression which is used for the blockage mechanism, a number of different rate forms such as

logarithmic or exponential can be obtained.

At low oxidation temperatures, many metals exhibit a high initial rate with a gradual decrease to very low levels. This type of behavior can be described by an inverse or direct logarithmic expression such as

$$X = k_d \log(t + t_0) + A$$

for direct, and

$$\frac{1}{X} = B - k_i \log t$$

for the inverse. k_d and k_i represent the rate constants. A , B and t_0 are also constants. These relationships can be developed for various rate-determining mechanisms such as transport of electrons or ions due to electric fields across the film, chemisorption or cavity formation in the film.

In each of the rate expressions discussed here, there is a rate constant which is usually a function of temperature. It has been shown empirically that the temperature dependence of these parameters follows an Arrhenius-type equation,

$$k = k_0 \exp(-Q/RT)$$

where Q is an activation energy, R the gas constant and T the absolute temperature. The pre-exponential factor is usually independent of temperature. With the exception of the parabolic mechanism, a detailed physical interpretation of k_0 and Q is difficult and generally not available. In the Wagner theory of oxidation, the parabolic rate constant is shown to be a function of ion diffusivity. Q is then related to the energy required for an ion to make a jump to another lattice position.

The particular reaction kinetics that are observed depend almost entirely on the structure of the growing oxide film. If, for example, a porous oxide is formed, diffusion through the oxide is rapid and a

surface reaction would be the rate controlling step. On the other hand, a dense, adherent oxide is likely to be a barrier to diffusion with this being the rate controlling step. There is no rigorous theory which can be used to determine the character of the oxide that will form during oxidation. There are, however, a number of criteria which have been presented in an attempt to predict whether a material will form a protective or nonprotective oxide. Two of the more important ones are the Pilling-Bedworth ratio (7) and the thermal expansion mismatch.

The Pilling-Bedworth rule states that if the oxide products occupy a lesser volume than the solid from which they are formed, a permeable product layer results and the reaction rate is independent of time. If, on the other hand, the reaction products occupy a greater volume, the reaction rate is controlled by passage of the reactants through the oxide layer. If the product layer is adherent and if diffusion is slow, the rate of attack may fall off rapidly to a negligible level. This rule is applicable only for the case of inward diffusion of oxygen through the oxide. The Pilling-Bedworth ratio is only useful as a guide since there are a considerable number of materials for which it does not hold.

Another factor to be considered is the difference in the coefficients of thermal expansion of the oxide and the substrate. If these are very different and thermal cycling is involved, the product layer may flake off the surface of the solid reactant.

Neither of these principles indicates in terms of fundamental, structural considerations whether the oxide will form a protective or nonprotective film.

III. Relevant Glass Theory

In order for silicides to be protective in an oxygen atmosphere, it appears that the formation of a glassy adherent oxide film is required. Once this film is formed, it inhibits further reaction by acting as a barrier to oxygen or metal diffusion. A knowledge of the basic structure of the glass is therefore required in order to elucidate the mechanism involved in the oxidation reaction.

For the glass that might form on silicides, there are three particular areas of glass theory that are of concern. One is the knowledge of the basic structure of vitreous silica. Also, since there are metal cations in the silicides, a knowledge of their extent of participation in the glass is required. And lastly, the effect of impurities and imperfections on the crystallization of glasses.

The most widely accepted theory of the structure of glass is that proposed by Zachariasen (8) and known as the random network theory. This theory pictures the basic atomic structure of amorphous silica as one in which each silicon atom is surrounded by four oxygen atoms as in the crystalline forms of silica and silicates. The structure is continuous and three dimensional with the tetrahedra arranged in a random manner. Amorphous silica exhibits the same short range order as the crystalline forms of silica but does not have their long range order.

The structure of the tetrahedron has been confirmed by X-ray diffraction studies. The average Si-O interatomic distance is 1.62 Å (9). The chemical bond appears to be of mixed character, partly ionic and partly covalent. Assuming a regular tetrahedron, the O-O distance is 2.65 Å (9). A value of 3.00 Å is obtained for the average Si-Si distance (10). In most crystalline phases of silica, the oxygen atom lies on a straight line between the silicon atoms. In vitreous silica,

the variable orientation of the tetrahedra results in a Si-O-Si angle of $143^\circ \pm 17^\circ$ (10). The oxygen in the tetrahedra are either bridging or non-bridging. In bridging, the oxygen links two tetrahedra while a nonbridging oxygen is connected to only one. The silica structure is a rather open one containing holes or interstices between the randomly linked SiO_4 tetrahedra. Consequently, the density of the silica glass (2.2 gms/cm^3) is less than that of quartz (2.65 gms/cm^3) where the tetrahedra are uniformly arranged. These holes can also accommodate various cations such as alkali or alkaline earth ions in forming silicate glasses.

A major factor in the ability of a silicide to form an impervious glass is the compatability of the two oxides that may form during oxidation. In general, there are three classes into which oxides fall depending on their function in the glass structure. A network-forming oxide is one which, when melted and cooled, has the ability to form a continuous three-dimensional random network. The two other classes are incapable of building up a continuous network but can take part in the glass structure. Sodium oxide is a good example of a modifying oxide. An intermediate oxide is one which usually is not capable of forming a glass but can take part in the glass network.

A concept that is useful in determining the role an ion will play in a glass structure is the ionic field strength (11).

$$F = Z/r^2$$

where Z is the ion valence and r the ionic radius. The field strength is a measure of the "ordering" effect which a cation can exert on neighboring ions. Table 1 (11) shows some of the ions commonly found in glasses along with their ionic radius, field strength and role in glasses. These data indicate that the ions which are network formers have high field strengths while network modifiers are larger ions with

Table 1

Ionic Radius and Field Strength of Cations Present in Glass (11)

<u>Ion</u>	<u>Ionic Radius, Å</u>	<u>Field Strength, Z/r^2</u>	<u>Structural Role in Glass</u>
Si ⁴⁺	0.41	23.8	Network former
Ti ⁴⁺	0.68	8.7	Intermediate
Zr ⁴⁺	0.80	6.3	Intermediate
Mg ²⁺	0.65	4.7	Network modifier
Ca ²⁺	0.99	2.04	Network modifier
Na ⁺	0.95	1.11	Network modifier
K ⁺	1.33	0.57	Network modifier

lower field strength.

Another important factor in the ability of a glassy film to afford oxidation protection is whether crystallization will occur. At elevated temperatures, impurities, dust, scratches, or flaws in the glass can catalyze the formation of the thermodynamically more stable crystalline forms of silica. The uncontrolled growth of crystalline phases during the preparation of glasses is highly undesirable. These phases can have a markedly different thermal expansion coefficient from the glass which can lead to high stresses and possible fracture during cooling.

There are a number of factors that influence the crystallization process. A lower interfacial energy between the two phases and similar structure and lattice parameters favor nucleation. In addition, a low activation energy for diffusion is required to allow crystal growth.

The crystalline forms of silica that are stable in the temperature region being considered are quartz, tridymite and cristobalite. A summary (12) of their stability ranges is shown in Table 2. When fused silica is heated at temperatures above 1000°C, cristobalite is normally favored. The presence of impurities, however, can cause one of the other modifications to form.

Titanium dioxide, a likely oxidation product of titanium silicides, is one of the best known examples of a nucleation catalyst. It is used in concentrations of 2 to 20 percent to promote controlled crystallization in the production of glass-ceramics (13). Although the mechanism involved in this crystallization process has not yet been fully explained, there are two views currently being considered (13). One is that there is a separation of submicroscopic crystalline particles which act as nucleation sites. The more accepted hypothesis is that initially two liquid phases are formed. The titania-rich droplets can then act as

Table 2

Phases of Silica (12)

<u>Form</u>	<u>Stability Range, °C</u>
Quartz _p low	to 573°
Quartz _p high	573 - 867°
Tridymite (9 forms)	to 1470°
Cristobalite _p low	to 272°
Cristobalite _p high	272 - 1723°

nucleation sites for the matrix or the phase itself may crystallize homogeneously. The formation of two liquid or glass phases appears reasonable since the interfacial energy in such a system might be almost zero.

The two most common analytical techniques used in exploring glass structure are X-ray diffraction and infrared spectroscopy. In addition to these two, nuclear magnetic resonance, neutron diffraction and electron microscopy are finding increased usage. In this study, X-ray diffraction, infrared spectroscopy and electron microscopy are used.

The lack of long range order in glasses prevents formation of sharp diffraction maxima and thus limits the application of the X-ray method. A typical X-ray diffraction pattern of a glass shows only diffuse haloes. Special methods (14) have been developed that allow the determination of the radial distribution functions and electron densities with respect to a selected central atom. This information is much less detailed than that normally obtained for crystalline solids. In particular, the symmetry and extent of the short range order are not well resolved by the diffraction method. Where crystalline growth occurs as in glass ceramics the usual diffraction method provides useful information.

The infrared spectrum depends primarily on the near-neighbor interactions and could, therefore, be capable of providing additional information. Since there is no rigorous theory of vibrational spectra of random lattices, much of the interpretation of experimental results has to be by inference and analogy.

A complete interpretation of the infrared spectrum of amorphous silica has not yet been developed. The major absorptions are located at 1100, 800 and 465 cm^{-1} (15). For a more detailed discussion of the infrared spectrum see Appendix A.

IV. Survey of the Literature

A. Introduction

There are four areas in the literature which are relevant to an understanding of the mechanism for the oxidation of bulk TiSi_2 . These are: the oxidation of bulk silicides, in particular MoSi_2 ; the oxidation of silicide coatings containing TiSi_2 ; the oxidation of silicon, which forms a silica film that is an excellent barrier to diffusion; and the reactions between bulk TiO_2 and SiO_2 , the likely products in the oxidation of TiSi_2 .

B. Bulk TiSi_2 Studies

Little work has been done on the intrinsic oxidation behavior of bulk titanium silicides. Samsonov (16) describes the results of an experiment in which TiSi_2 was heated to 1200°C over a four hour period. The weight gain observed was only 0.3 mg/cm^2 . An adherent oxide film was formed. The author speculates that the protective nature of this film is due to the formation of an eutectic mixture of titanium silicates. No mention is made of the sample density, quality of surface or any of the other variables significant in oxidation studies.

C. Bulk MoSi_2 Studies

The silicide whose oxidation has been studied most extensively in bulk form is MoSi_2 . Wirkus and Wilder (17) have recently summarized the oxidation studies on MoSi_2 . They show two distinct temperature regions where a characteristic oxide is formed.

Measurable oxidation begins at about 300°C for both bulk and powdered MoSi_2 . At temperatures of 300 - 600°C , a duplex oxide of MoO_3 and SiO_2 forms. This region has been termed the "pest" since the oxide spalls from the silicide surface. The silicide is not protective in this temperature range with deterioration occurring at a rapid rate.

Berkowitz-Mattuck et.al. (18) have carried out an extensive investigation of the oxidation of MoSi_2 in the temperature region 450-650°C. The authors studied the oxidation of polycrystalline and single crystal samples made using a zone refining technique. The polycrystalline samples were found to deteriorate when exposed to oxygen, but not nitrogen, carbon dioxide, carbon monoxide or argon. X-ray analysis indicated MoO_3 and SiO_2 were present as the oxidation products. The observed rate of disintegration was extremely sensitive to changes in the oxygen pressure.

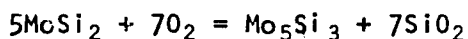
One of the major characteristics of pesting is the increase in the number of cracks in the substrate as oxidation proceeds. These cracks are of all kinds, some occurring within single grains and others across or along grains. Single crystal samples of MoSi_2 did not exhibit pest. Oxygen solubility in MoSi_2 is extremely low with no change observed in the lattice parameters during oxidation.

The authors indicate that the physical nature of the MoSi_2 may be the significant factor in the "pest" phenomena. Materials which can be prepared crack free, such as Mo_3Si , do not pest, while those which are difficult to prepare free of cracks, do. WSi_2 (650-2150°C), Nb_5Si_3 (500-1150°C) and Mo_5Si_3 (500-800°C) are materials that do contain cracks and also show pest in an intermediate temperature region.

If the diffusion of oxygen through the oxide to the MoSi_2 is involved in the reaction sequence, the newly forming oxide in a crack would exert considerable pressure since the volume expansion would be about 200 per cent. This would tend to propagate the crack and result in sample deterioration.

At temperatures above 600°C, the volatility of MoO_3 becomes appreciable. A two-stage mechanism has been proposed for this region. In

the initial stage of oxidation, both oxides are formed. The MoO_3 volatilizes, leaving a relatively pure silica film. The oxygen activity at the substrate-oxide interface is considerably reduced because of the dense, impervious nature of the oxide. Under these conditions, Searcy (19) claims that the reaction



is thermodynamically favored. The Mo_5Si_3 is found in a layer directly below the protective SiO_2 film. This is confirmed by X-ray diffraction and weight change studies. If MoO_3 and SiO_2 were formed, a weight loss would be observed due to MoO_3 volatilization. On the other hand, formation of SiO_2 and the lower silicide would show a weight gain. This latter case is what is observed.

The rate determining step appears to be diffusion through the oxide film. Since Mo_5Si_3 forms below the oxide surface, the diffusion of silicon through this layer may be the significant rate determining factor. Wirkus and Wilder discuss this possibility and conclude that the silicon mobility is much larger in the silicide than is the oxygen in SiO_2 .

D. Coating Studies

An example of a typical method of forming a silicide coating on a refractory metal is the pack cementation technique (3). The metal is surrounded by silicon powder in a retort. Usually about 10 wt. percent NaF is present as an activator. The reaction temperature is about 1200°C for times of 4-8 hours. At this temperature, the fluoride volatilizes, reacts with the silicon to form a gaseous silicon halide which then reacts with the metal. The silicon diffuses in, while the halogen is recycled to continue the reaction. Final coating thickness is usually 3 to 4 mils.

The vacuum slip process (5) is a variation wherein a slurry of fine metal particles, halide activator, polyisobutylene binder and toluol is either sprayed, painted or in some other way applied to the metal surface. After drying, the sample is placed in a retort and carried through a cycle similar to that in the pack cementation process.

The simplest coating system can be obtained by straight siliciding of the tantalum or columbium metal. It has been found (3), however, that on oxidation $TaSi_2$ and $CbSi_2$ form nonprotective oxide scales. For this reason, other materials are added to the silicon powder during the coating preparation to improve the oxidation resistance. Some of the materials which give favorable results when used by themselves or in combination with each other are silicides of titanium, chromium, vanadium and molybdenum. Alternatively, the substrate metal may just be alloyed with these metals.

The most useful and one of the few fundamental studies aimed at determining the composition of the oxide film formed during oxidation of silicide coatings on tantalum was carried out by Bracco, et.al. (4). Two coating systems and two metal substrates were used in this work. The coatings were prepared by straight siliciding and siliciding with 90Ti-10W in the pack. The substrate materials were tantalum and T-222 alloy ($\sim 88Ta-2.7Hf-9W$). The analytical techniques used for studying the oxide film that was formed on oxidation were X-ray diffraction and electron microprobe analysis.

When the samples that were straight silicided were oxidized, the major oxidation product was found to be Ta_2O_5 . At oxidation temperatures of 2800°F (1538°C) $\alpha-Ta_2O_5$ predominated, while at 2500°F (1371°C), the $\beta-Ta_2O_5$ form was the major product. SiO_2 (α -cristobalite) was present

in trace amounts when the tantalum-based silicide coating was oxidized at 2800°F (1538°C), while none was found when T-222 samples were similarly treated. Some shifts were noted in the reflectance peaks of Ta₂O₅ which may indicate SiO₂ solution since thermodynamically SiO₂ should be present.

A somewhat different situation resulted in the case where a Ti-W-Si coating system was used. TiO₂ (rutile) and SiO₂ (α-cristobalite) were the major oxide phases formed at 2500°F (1371°C). Tantalum oxides were not found. As in the straight tantalum work, no SiO₂ was found in the 2800°F (1538°C) samples, TiO₂ (rutile) being the main product. In this case, the lack of indication of SiO₂ may be due to its being amorphous and, therefore, not indicated because of interference from the strong orientation in the TiO₂ reflections.

Wimber and Stetson (5) have reported results on a more complex silicide coating formed on tantalum T-222. This coating contained 15Ti-35W-15V-35Mo where the values are in wt. percent. When this coating was oxidized at 2400°F (1316°C) for 400 hours, three oxide phases were observed under microscopic examination. One appeared white, the other light gray and the third dark gray. An electron microprobe run parallel to the surface indicated that the white phase was TiO₂. The (110) plane was found to be oriented parallel to the sample surface. The light gray phase contained 4 to 6 percent titanium while the dark gray phase contained no titanium. No silicon appeared in the white phase. The light gray contained 10 percent and the dark gray 20 percent. The authors suspect that the dark gray phase was slightly impure, partially devitrified SiO₂ while the light gray phase was a titania-silica glass.

E. Binary TiO_2 - SiO_2 System

There has been little work done on interactions in the binary TiO_2 - SiO_2 system. The first phase equilibrium study was reported by Bunting (20). He shows the phase diagram as a simple eutectic with no compounds and no solid solubility. The eutectic was given at 1540°C for 10.5 wt. percent TiO_2 .

A later, more detailed study was carried out by Ricker and Hummel (21). They report the revised phase diagram shown in Figure 1. Their data relocates the eutectic composition at 21 wt. percent TiO_2 with the same eutectic temperature of 1540°C . In addition, considerable solid solubility is indicated at both the high and low silica concentrations. The maximum values are approximately 10 percent TiO_2 in high cristobalite and approximately 24 percent silica in rutile at the eutectic temperature. At 1500°C , a heat treatment time of 10 hours is reported sufficient to produce equilibrium, while at 1350°C , 30 hours is satisfactory. At 1350°C , X-ray data gave evidence of limited solubility. At 1000°C , even after 168 hours heating, no conclusions could be drawn since equilibrium conditions were probably not obtained.

The refractive index of the cristobalite solid solution was observed to increase as more TiO_2 was included. The average refractive index of a solid solution containing 9 percent TiO_2 was 1.490.

Ricker and Hummel also prepared TiO_2 - SiO_2 binary glasses by heating samples of the desired composition to 1700°C in platinum and quenching. The glasses were light bluish-gray, transparent when 2-3 mm. thick and opaque at greater thicknesses. The refractive indices of the glasses were given as:

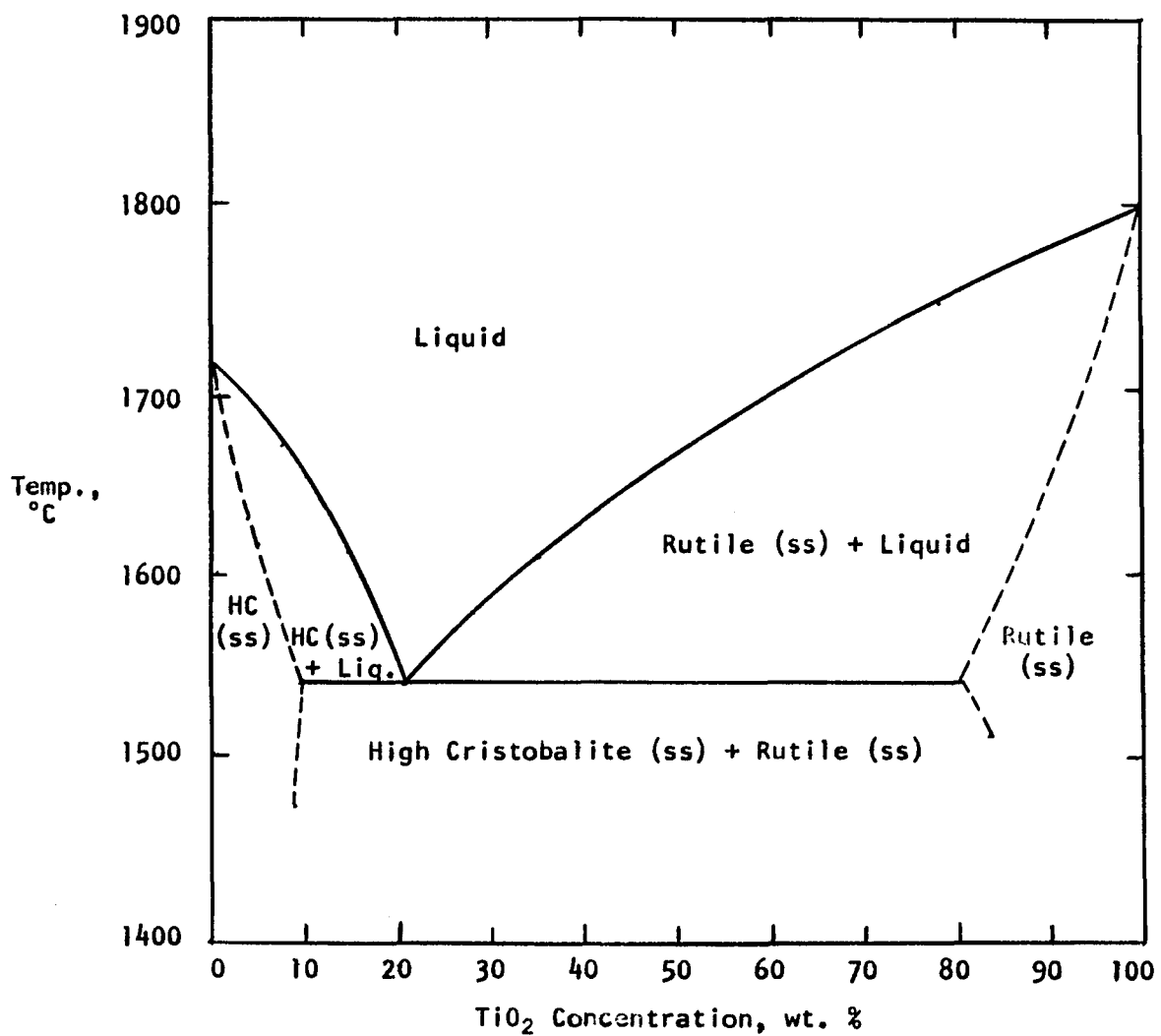


Figure 1. TiO_2 - SiO_2 Phase Diagram (21)

<u>TiO₂ Conc., Wt. %</u>	<u>Refractive Index</u>
9	1.493
13	1.503
20	1.538
25	1.556

The refractive index of pure silica is reported as 1.46. These glasses were annealed at 1575°C for 1.5 hours and then quenched. The samples containing 9 and 13 percent TiO₂ analyzed as cristobalite with extremely small specks of what appeared to be TiO₂. The 20 percent sample remained essentially a glass with only a slight trace of unidentified crystals with the 25 percent sample containing large crystals of rutile.

An important conclusion of this study is that at temperatures over about 1000°C, 10 wt. percent TiO₂ can be dissolved in SiO₂. The resulting solid solution is retained when cooled to room temperature

As indicated earlier, titanium is normally classified as an intermediate ion, i.e., although not usually capable of forming a glass, it can take part in the glass network. Because of its size, it usually assumes a coordination of 6. In order to take part in the silica network, the required coordination would be 4. Many ions exhibit a decrease in coordination as the temperature is increased. Titanium then could assume the required coordination of 4 at the temperature at which solution occurs. Quick cooling could then freeze the dissolved titanium in the network forming position.

The results of Ricker and Hummel (21) do not indicate whether the TiO₂-SiO₂ glasses with less than 10 wt. percent TiO₂ are homogeneous or whether amorphous phase separation has occurred. Two phase separation has been observed in the MgO-SiO₂ and CaO-SiO₂ systems but not in the

$\text{Na}_2\text{O-SiO}_2$ and $\text{K}_2\text{O-SiO}_2$ systems (22).

F. Oxidation of Silicon

1. Structure of the Oxide Film

In delineating the mechanism for the oxidation of silicides, it is worthwhile to consider a comparison with the oxidation of silicon which has been studied in great detail in recent years. All of the latest studies on the oxidation of pure, single crystal silicon indicate that when "clean" surfaces are used, the SiO_2 film that is formed is amorphous. The quality of the amorphous film, in terms of density and defects, is determined by the nature of the surface preparation, oxidation conditions and type of oxidant. From the standpoint of oxidation protection, a high density film is desired since this shows a lower growth rate.

Pliskin and Lehman (23) have carried out an extensive transmission infrared study on the structure of SiO_2 films formed by thermal oxidation and evaporation techniques. As indicated earlier, the infrared spectrum of bulk amorphous SiO_2 shows absorptions at 1100, 800 and 465 cm^{-1} . (See Appendix A). With a bare silicon wafer in the reference beam, Pliskin and Lehman report a strong Si-O stretching band at 1090 cm^{-1} . The half-width and position of this band was strongly influenced by bonding character, stoichiometry, density and porosity of the film. At 1250 cm^{-1} a slight bump in the broad 1090 cm^{-1} peak was observed. The Si-O-Si bending vibration at 450-460 cm^{-1} was not discussed since it behaves in the same way as the 1090 cm^{-1} peak.

A typical, dense SiO_2 film with a thickness of 1 μ had absorption peaks at 1093 and 805 cm^{-1} . A lower density pyrolytic oxide film showed bands at about 1080-1085 cm^{-1} , and 813 cm^{-1} . Films with greater porosity

and bond strain show even greater shifts than those indicated above. In comparing oxide films, comparable thicknesses are required since half-widths and band positions vary slightly with thickness.

Murray and Goldsmith (24) in a reflection study of SiO_2 on silicon, showed the effect of film thickness on peak position. Reflection maxima are observed at 1280 and 1120 cm^{-1} with corresponding minima at 1260 and 980 cm^{-1} . The authors indicate that increasing the thickness from 1000 to 10,000 Å shifts the reflection peak from 1070 cm^{-1} to 1120 cm^{-1} .

Sato and Shibata (25) have studied the restrahl reflection spectrum of amorphous SiO_2 grown on silicon and presented a mechanism to explain changes in peak position with changes in thickness. The authors also compare the spectrum for amorphous SiO_2 with that of quartz and indicate that the knowledge of the spectral reflectivity of the amorphous form is in its infancy.

A reflectance attachment with an angle of incidence of 10° was used in the study. The surface and backside reflectivities of the sample were measured. The backside reflectivity was obtained by removing the oxide on the back of the sample and having the infrared beam incident on that surface. Film thicknesses were smaller than the "reflection depth" at the silicon surface which should be about 1/2 the wavelength of the incident radiation (5000-7000Å).

The Si-O stretching band at 1100 cm^{-1} and the Si-O bending band in the 470 cm^{-1} region were both observed while the Si-Si stretching bands at 800 and 775 cm^{-1} and the Si-Si bending band at 540 cm^{-1} were either missing or very weak. These latter Si-Si bands are usually quite clear in quartz.

The reflection spectra obtained by Sato and Shibata are similar to

that obtained by Murray and Goldsmith (24). Peak position decreased from 1100 cm^{-1} at $5200\text{ \AA}$ to 1060 cm^{-1} at $1000\text{ \AA}$. In addition, the reflection intensity decreased until at $1000\text{ \AA}$, the curve was almost flat. At less than $750\text{ \AA}$, the peak became an absorption peak. The back reflection gave, in all cases, an absorption peak.

Sata and Shibata suggest that the shift in peak position is due to silicon with dangling bonds on the surface. If Si represents silicon bonded to only three oxygen, $\text{Si}^\cdot$ two and $\text{Si}^{\cdot\cdot}$ one, then the absorption frequencies would be

$$\nu(\text{Si}) > \nu(\text{Si}^\cdot) > \nu(\text{Si}^{\cdot\cdot}) > \nu(\text{Si}^{\cdot\cdot})$$

As the surface of the oxide is approached from within the oxide, the number of "unsaturated" silicon atoms would increase. As the film gets thinner, the silicon with dangling bonds would have a greater effect and the band would be observed at a lower frequency. The backside data show no shift which the authors claim is consistent with the model since there would be no reason to find silicon with dangling bonds at the silicon-silica interface.

Deal (26) reports the following data on SiO_2 films on silicon obtained from thickness and weight change measurements.

<u>Oxidant</u>	<u>Temp., °C</u>	<u>Density, g/cm³</u>
Dry O ₂	1000	2.27
	1200	2.24
Wet O ₂	1000	2.18
	1200	2.21
Steam	1000	2.08(2.00-2.20)
	1200	2.05(2.00-2.20)

Ing, et. al. (27) report on a permeation study designed to determine the imperfections in a thermally grown film on silicon. The authors etched a hole (area $\sim 0.01 \text{ cm}^2$) in an SiO_2 film with HF. Upon exposure to chlorine at 800°C , the silicon in the hole was vaporized as SiCl_4 . Since the SiO_2 film is not attacked by the chlorine, an SiO_2 window is formed at the other end of the hole. A pressure drop was then applied across the film and the permeation rate measured. For films $5000 \text{ \AA}$ thick, a (ΔP) of 200 mm was used, while for films of $15,000 \text{ \AA}$ thick, 760 mm was used. Results were categorized as:

<u>Permeation Constant, $\text{cm}^3\text{-cm/sec-cm}^2\text{-cm Hg}$</u>	<u>Mechanism</u>
10^{-3} to 10^{-5}	Flow through microcracks and crystalline boundaries
10^{-7} to 10^{-10}	Flow through microchannels
10^{-15}	True diffusion and permeation

The bulk of the results in the study fell in the 10^{-7} to 10^{-10} range or flow through microchannels. In some of the films, where crystal-like growth appeared, the permeation rate was $\sim 10^{-4}$. These crystallites varied in diameter from 4×10^{-4} to $3.3 \times 10^{-3} \text{ cm}$. When the entire film was etched away, the silicon appeared pitted where the crystals were observed in the film. In addition, it was found that the permeation rate varied with the base used.

In contrast to the single crystal studies, Evans and Chatterji (28) carried out a study on the oxidation of silicon formed by melting powdered silicon in a thoria-lined alumina crucible. The oxidation product upon analysis by X-ray was found to be transparent cristobalite. Evans and Chatterji also observed that silicon reacts with nitrogen at $1200\text{-}1360^\circ\text{C}$ to form Si_3N_4 . Weight gains as high as 1 mg/cm^2 were observed after three

hours in pure N₂.

2. Film Growth Mechanism

In determining the mechanism for the oxidation of silicon, three distinct temperature regions are considered. The first is the range from room temperature to 500°C where no noticeable oxidation occurs. In the region from 500-900°C, the oxidation kinetics are apparently linear, while from 900-1200°C, the kinetics are parabolic.

An excellent summary and interpretation of the rate data on silicon oxidation was recently presented by Deal and Grove (29). Where other authors considered a single "rate controlling step" for each temperature region, Deal and Grove used a combined mechanism considering all the steps in a single model. The basic assumption was made that the film thickness was large enough so that the effect of space charge conduction was negligible.

In developing the general rate expression, four steps were considered in the reaction sequence. These were: gas phase diffusion of oxygen to the oxide surface; adsorption of oxygen onto the oxide film; diffusion through the oxide film; and reaction at the oxide-silicon interface. Using a suitable mathematical expression for each step, the general rate expression

$$X^2 + AX = B(t + \tau)$$

where X = weight gain or oxide thickness, t = time, B = parabolic rate constant, B/A = linear rate constant, τ = constant related to initial condition, was obtained. B is directly related to the effective diffusivity through the film and B/A to the reaction rate constant and gas phase mass transfer coefficient.

Deal and Grove determined the importance of the various parameters

in the above relation. An oxidation study was carried out with dry oxygen (less than 5 ppm water) over the temperature range 700-1200°C. The silicon was Czochralski pulled (single crystal pulled from the melt), p type, boron doped with an (111) surface. Multiple beam interference techniques were used to determine the oxide film thickness.

For the case with dry oxygen, it was found that none of the curves of X versus t extrapolated through the origin. At all temperatures, a value of X of $230 \pm 30 \text{ \AA}$ was obtained at $t = 0$. At 700°C, where the oxidation was extremely slow, an extrapolated value of $X = 210 \text{ \AA}$ was obtained from the linear part of the curve. This value was adopted as the value of X_i , the initial condition.

The values they obtained for B , B/A and τ are shown in Table 3. A plot of $\ln B$ vs. $1/T$ indicated a diffusion activation energy of 28.5 kcal. This compares with a value of 27.0 kcal obtained by Norton (30) and 71.2 kcal by Sucof (31) for the diffusion of oxygen through fused silica. A plot of $\ln B/A$ vs. $1/T$ also gave a straight line with an activation energy of 46.0 kcal.

The parabolic rate mechanism found in the oxidation temperature region 900-1200°C indicates that the diffusion of a particular species is the rate controlling step in the reaction. In this system, the possible diffusants are: the silicon atom or ion; the oxygen atom or ion; or the oxygen molecule. Marker studies (32,33) have shown that some form of oxygen is the diffusing species. The data of Flint (34) indicate that the parabolic rate constant is directly proportional to the oxygen pressure. These results led Deal and Grove (29) to the conclusion that O_2^- is the diffusing species.

The mechanism by which the oxygen is transported through the silica

Table 3

Silicon Oxidation Rate Data of
Deal and Grove (29)

<u>Temp °C</u>	<u>A(μ)</u>	<u>B(μ²/hr)</u>	<u>B/A(μ/h)</u>	<u>τ(h)</u>
1200	0.040	0.045	1.12	0.027
1100	0.090	0.027	0.30	0.076
1000	0.165	0.0117	0.071	0.37
920	0.235	0.0049	0.0208	1.40
800	0.370	0.0011	0.0030	9.0
700			0.00026	81.0

film is not understood. Sufov (31) proposed that the mechanism of oxygen diffusion in silicate glasses and non-stoichiometric silica involves the rupture of a single oxygen bond to silicon and that the diffusion occurs by interstitial motion through the voids formed in the lattice. A calculation shows that at least 50 kcal per mole is required to remove an oxygen from the lattice. Since two bonds must be broken for vacancy diffusion, the activation energy would be at least 100 kcal/mole. This would appear to indicate interstitial diffusion since the experimental value obtained was 71.2 kcal/mole. Similar activation energies are obtained for oxygen diffusion in soda lime glasses indicating a similar mechanism.

Ligenza (35) carried out a study on the effect of crystal orientation on the oxidation rate of silicon in high pressure steam. The kinetics were linear and directly proportional to the steam pressure. The three crystal orientations studied were the (110), (311) and (111) faces.

It was found that the reaction rate at any temperature was greatest for the (110) face followed by the (311) and then the (111). The largest difference in rate observed was approximately 50 percent. The activation energy was found to be identical within experimental error for the (311) and (111) faces, while for the (110) face, the activation energy was smaller. The pre-exponential factor varied as follows: (110):(311):(111), 1.00:1.71:1.3. The ratio of k_{111}/k_{110} was found to be equal to 0.8 at all temperatures.

Ligenza, in an attempt to explain the orientation results, develops an expression which indicates that the rate of film growth is proportional to the pressure and the concentration of Si-Si sites on the

surface. This site concentration will obviously be a function of crystal orientation. Correlation of the reaction rate with orientation was carried out by drawing pictures of the various atomic configurations and estimating the number of Si-Si sites available for reaction. A qualitative confirmation was made with the experiments.

V. Properties of the Titanium Silicides

The titanium silicides are part of a class of materials commonly called "metal-like" refractory compounds. This classification is based on their external and internal resemblance to metals.

The phase diagram for the titanium-silicon system is shown in Figure 2 (36). Three compounds are indicated. These are TiSi_2 , TiSi and Ti_5Si_3 . A summary of the properties of these materials as given by Samsonov (37) is shown in Table 4.

Little is known at the present time about the nature of the chemical bonds in titanium silicides. In titanium disilicide, the crystal structure is such that no direct metal-metal bonding is possible. The bonds that give rise to the properties of the disilicide are those of metal-silicon and silicon-silicon. In the lower silicides, it appears that the metal-metal bond does influence the properties of the material, as indicated by their higher melting points. One of the interesting properties of the titanium silicides is their low resistivities. The data in Table 4 show values of 16.9 for TiSi_2 , 63 for TiSi and 55 micro-ohm-cm for Ti_5Si_3 . The resistivity of titanium metal is 55.0 micro-ohm-cm (38). It has been suggested (39) that electron transfer occurs from the silicon to the titanium giving rise to unsynchronized resonance with the result that the silicon atom is in the metallic state.

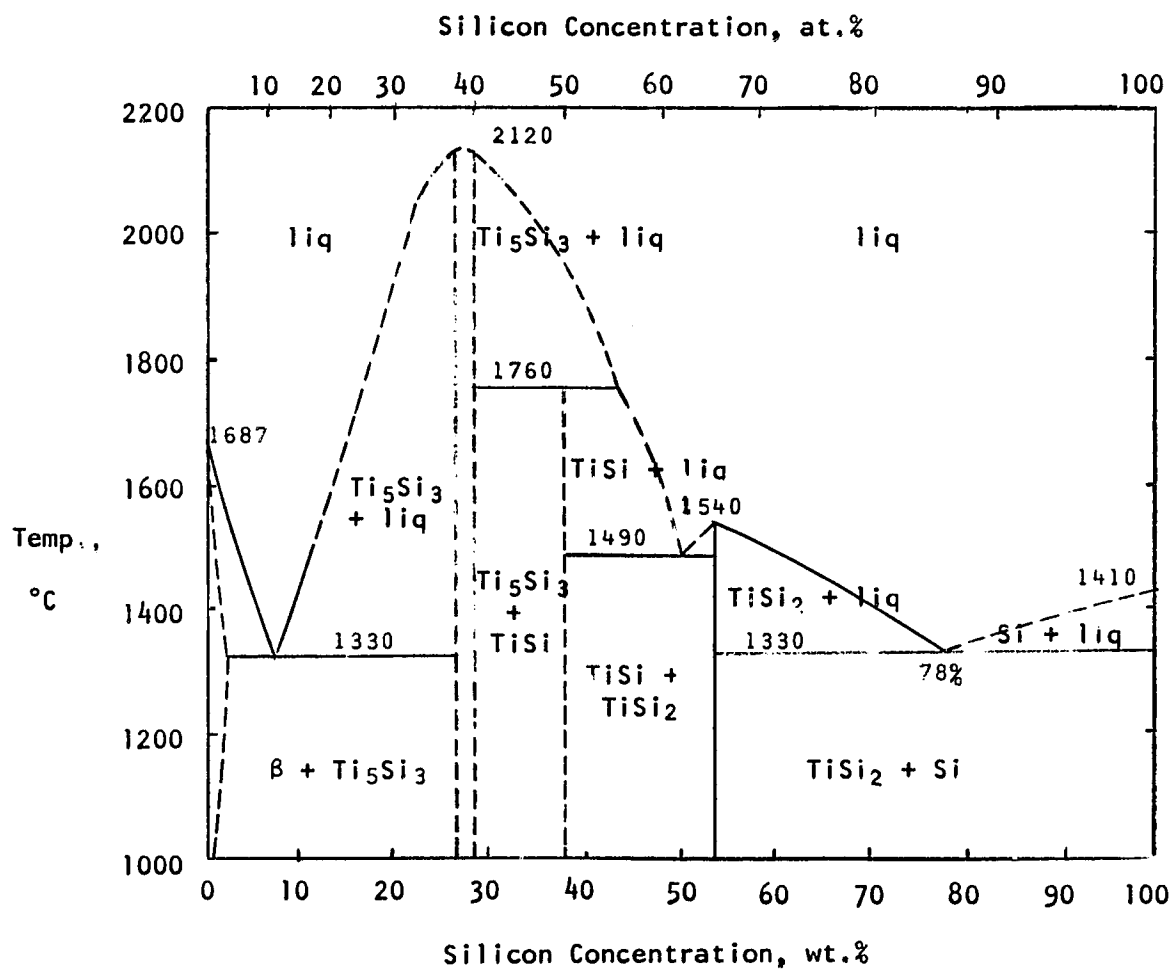


Figure 2 The Titanium - Silicon System (36)

Table 4

Properties of the Titanium Silicides (37)

	<u>TiSi₂</u>	<u>TiSi</u>	<u>Ti₅Si₃</u>
Molecular Weight (37a)	104.08	75.99	323.77
Silicon Content, wt.%	53.98	36.97	26.03
Melting Point, °C (37b)	1460-1540	1920	2120
Microhardness, kg/mm ² (37c)	892	1039	986
Crystal Structure (37d)	orthorhombic	orthorhombic	hexagonal
Space Group	D _{2h} ²⁴ - Fddd	C _{2v} ¹ - Pm2m	D _{6h} ³ - C6/mcm
Lattice Constant, Å	a = 8.236 b = 4.773 c = 8.523	a = 4.97 b = 3.62 c = 6.48	a = 7.465 c = 5.162
Density X-ray, gms/cm ³	4.13	4.21	4.32
Density, pycnometer, gms/cm ³ (37e)	4.39	-	-
Coefficient of thermal expansion α, (1/°C) · 10 ⁶ (37f)	10.5 (20-1070°C)	8.8 (20-370) 10.4 (370-1070)	11.0 (170-1070)
Specific resistance, microhm·cm at 20°C (37g)	16.9 ± 0.5	63 ± 6	55 ± 4
Hall constant R _H , (cm ³ /coul) · 10 ⁻⁴ (37h)	- 0.63	- 0.43	- 0.27
Magnetic susceptibility, (per mole) · 10 ⁶ (37i)	+ 112 + 129	+ 55	+ 810

VI. Experimental

A. Sample Preparation

The titanium silicide wafers used in this study were prepared using the techniques of powder metallurgy (40). In the initial phase of the study, TiSi_2 powder from CERAC, Inc. was used. This material was -325 mesh with a minimum purity of 99.6 percent. A typical analysis as supplied by the manufacturer is given in Table 5. These data indicate a silicon excess of 0.68 percent.

The pressing of one inch diameter wafers directly from the purchased powder proved quite difficult. Pressures of 10-50 tsi were investigated using a hardened steel die. Invariably, the samples cracked on ejection. A number of binders were evaluated using lower pressures. A satisfactory procedure consists of slurring the titanium disilicide powder with a sufficient amount of a 5 percent polymethylmethacrylate solution in acetone to give a final dry mixture containing 0.1 percent polymer. After the powder is dried, one inch diameter wafers are pressed at 5-10 tsi. Sample thickness is approximately 0.1 inches.

Densification of the compacted wafer is carried out in two stages. In the presinter, the binder and any residual solvent are removed by heating in vacuum. The pressed wafer is supported on a high density alumina dish which is placed in an impervious silica tube. The tube is evacuated to 10^{-4} Torr and held for 0.5 hours. The temperature is slowly brought up to 900°C over a two-hour period. At the elevated temperature, the polymer "unzips" giving methacrylate monomer which is easily removed at the low pressure. There is no evidence of charring or carburizing of the polymer.

Table 5

Analysis of CERAC TiSi₂

	<u>Weight %</u>
Titanium	45.60
Silicon	53.80
Carbon	0.20
Iron	0.10
Oxygen	<u>0.30</u>
	100.00

The final sintering is carried out at 1375-1400°C and 5×10^{-5} for 15 minutes.

The faces of the sintered wafers are ground successively on diamond disks of medium, 30 micron and 6 micron coarseness. The ground wafers are then lapped with 6 and then 3 micron diamond paste.

In order to prepare wafers of better quality, two procedures for upgrading the purity of the silicide powder were investigated. The first consisted of reacting the CERAC TiSi_2 with a 10 percent NaOH solution. Dilute caustic dissolves the excess silicon but not the disilicide. The reaction is carried out at 40°C for two minutes. The slurry is immediately centrifuged and the caustic solution discarded. The silicide is then washed several times with water until a solution neutral to pH paper is obtained. The dried silicide powder is ground in a steel die, contacted with a 10 percent HCl solution for two hours to remove iron, centrifuged, washed with water and dried. The powder is sieved with the material passing through the 400 mesh being used for wafer preparation.

In addition to using the CERAC TiSi_2 , a number of wafers were fabricated from TiSi_2 powder prepared by direct reaction of titanium and silicon powder. Titanium powder from CERAC or titanium sponge from United Mineral and Chemical Co. was used in the reaction. The CERAC powder had a purity of 99.6 % while the UMC material was 99.9%. The sponge is ground in a hardened steel vial. The -325 mesh portion is removed, washed with dilute HCl, dried and used for reaction. The silicon powder was obtained from United Mineral and Chemical Co. and had a purity of 99.99%.

The required amounts of each material are weighed out in a plastic vial on a Mettler analytical balance. Usually, a slight excess of silicon,

0.1 wt. % is used. The vial containing the mixture is vibrated on a Spex Mixer/Mill for one hour. The mixed powders are pressed into one inch diameter wafers at pressures of 20-25 tsi. Reaction is carried out in a high density alumina crucible in a vacuum of 10^{-4} Torr. The crucible is surrounded by a tantalum susceptor in a two inch, induction heated, vertical tube furnace. The temperature is measured by sighting on the sample with an optical pyrometer.

Reaction begins when the sample temperature reaches about 900°C. At this point, the heating is discontinued. The reaction, however, is quite exothermic. If the mixture is heated too fast, the reaction temperature quickly exceeds the melting point of the reactants (1350°C) and the resulting molten mass adheres to the alumina crucible. Slow heating gives a controlled reaction with the temperature reaching a maximum of 1000°C. The final product is a slightly sintered, spongy mass of TiSi_2 . This is ground and the -400 mesh product used for wafer preparation.

Wafers of TiSi , Ti_5Si_3 and TaSi_2 are prepared in a similar fashion.

B. Oxidation Experiments

The oxidation experiments were carried out in vertical tube-type furnaces. The furnaces were constructed of JM 3000 firebrick and are 8 inches thick and 25 inches high, with a hole in the center for a 36 inch long mullite tube. The tube and its contents are heated by four uniformly spaced globars with an effective heating length of 20 inches. This arrangement gives a length of four inches near the middle of the tube where the temperature variation is less than 5°C. The temperature is measured and controlled by a thermocouple in the center of the tube extending from the bottom of the mullite tube to a point two inches

below the center.

One furnace was set up for studies below 1000°C, while the second was used for temperatures of 1000-1300°C. The lower temperature furnace is controlled by a Leeds-Northrup Speedomax H unit. Temperature variation is $\pm 2^\circ\text{C}$. A chromel-alumel thermocouple is used. The couple is calibrated by measuring the EMF in standard samples of silver (MP = 960.5°C) and lead (MP = 327.3°C). The temperature in the second furnace is controlled by a Wheelco model 404 controller. With this unit, the temperature variation is $\pm 5^\circ\text{C}$.

The atmosphere in the tube is a mixture of argon and oxygen. The oxygen partial pressures investigated were 0.2, 0.6 and 1.0. These were purchased directly from Matheson Inc. The gas is admitted through the bottom of the mullite tube with the rate controlled by a rotameter located at that point.

The samples were supported by a vitreosil (fused quartz) holder and suspended from the top of the furnace by a vitreosil rod into the region where the temperature variation was less than 5°C . No reaction was observed between the silicides and the vitreosil holder.

C. Analytical Techniques

1. Oxidation Rate Measurements

Oxidation rate data were obtained by periodically removing the sample from the oxidation furnace and recording the weight using a microbalance. An Oertling model 142 balance with a sensitivity of $\pm 2\text{ }\mu\text{g}$ is used. The sample weight can be reproduced with a precision of $\pm 5\text{ }\mu\text{g}$.

An attempt was made to measure the oxide film thickness using the VAMFO technique (41). This is essentially a non-destructive interference method for transparent films. It is commonly used to measure the thick-

ness of silica films grown on silicon. The method relies on determining the position of maximum or minimum interference by observation through a microscope. The method proved unsuccessful for the oxide formed on TiSi_2 . While the film is transparent and exhibits interference colors, the location of the interference maxima or minima could not be determined because the oxide is non-homogeneous and the substrate non-uniform.

The technique would be suitable if a more sensitive detector were used. A single sample scanned at Perkin-Elmer using a UV spectrophotometer showed typical interference peaks.

2. Metallography

Photomicrographs of the polished and etched silicides and oxide films were prepared with a Leitz model MM5 metallograph. The polished silicides were etched for 15 seconds in an etch consisting of:

- 5 parts hydrofluoric acid (by volume)
- 15 parts 5% chromic acid
- 40 parts 1% potassium permanganate
- 100 parts water.

The samples were observed under both ordinary and polarized light.

The oxide films were etched with "P" etch, a reagent commonly used in the modification of oxide films grown on silicon (23). This etch consists of:

- 15 parts hydrofluoric acid
- 10 parts nitric acid
- 300 parts water.

This reagent has been found (23) to etch pure SiO_2 films on silicon at a rate of $2 \text{ \AA/sec.}$, while impure SiO_2 films etch at a considerably faster

rate. A typical example is a phosphosilicate film which etched at 570 Å/sec.

A number of samples were sectioned in order to determine the vertical structure of the growing oxide. -200 mesh alumina powder was added to the usual epoxy resin to prevent rounding of the sample edges during polishing.

3. X-Ray Diffraction

X-ray diffraction scans were made on the silicide surface and the oxide film. The diffraction patterns were obtained with a Norelco Geiger counter X-ray spectrometer. $\text{CuK}\alpha$ radiation with $\lambda = 1.54050$ was obtained by passing the beam from a copper tube through a nickel filter. The surface of the wafer was scanned by inserting it directly in the sample holder. This non-destructive method allows for many measurements to be made on the same sample. A number of powder patterns were also prepared by grinding the finished wafer.

Several powder patterns were also obtained on the oxide film. In order to remove the oxide, a chlorine etch technique (42) used in studying the oxide formed on silicon was used. The powder patterns yield the same results as the simpler non-destructive method.

A number of mechanical mixtures of SiO_2 and TiO_2 of known concentration were prepared in order to determine the reproducibility of peak positions and intensity in the X-ray method. An approximate calibration curve for the concentration of TiO_2 in 0.5 inch diameter wafers was developed. The minimum amount of TiO_2 which can be detected is approximately 1%. Detailed results of this study are given in Appendix B along with X-ray data for TiSi_2 , TiSi , Ti_5Si_3 , TiO_2 and SiO_2 as reported in the ASTM Powder Diffraction File.

4. Infrared Spectroscopy

A more detailed analysis of the amorphous region of the oxide film was carried out using infrared spectroscopy. A Perkin-Elmer Micro Specular Reflectance Accessory was used in conjunction with 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 from 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.

The 621 instrument, a grating spectrophotometer with a frequency range of 4000 to 200 cm^{-1} , is a high resolution instrument. Frequency can be read to 0.1 cm^{-1} and slit width to 0.5 microns. Dry nitrogen is passed through the source-optics and monochromatic chambers to reduce interference of atmospheric carbon dioxide and water vapor when analyzing below 600 cm^{-1} . The equal compensating path of the reflectance unit also cuts down on this interference. Ordinate scale expansion is required for the thinner oxide layers. A more detailed discussion of the infrared method is given in Appendix A.

The infrared analysis of the bulk glasses was carried out using the KBr pellet method. The sample to be analyzed was ground on a Spex Mixer/Mill for about one hour. The powder was collected and $0.4 - 1.4\text{ mg}$ mixed for 30 seconds with 200 mg of KBr on a Spex Mixer. The powder was placed in a standard KBr pellet die, evacuated and pressed for 20 minutes at $20,000\text{ lbs}$. The KBr pellet was then placed in a holder and inserted directly in the sample beam.

5. Electron Microscopy

A standard replicating technique was used for studying the surface structure of both the TiSi_2 and the growing oxide film. A film of nitrocellulose from a 4 percent collodion solution was formed on the sample. The film was separated from the surface by initially forming a square around the desired region with cellophane tape. Breathing on the film supplied moisture which penetrated through the cellulose to the sample surface. The tape was peeled away, carrying the cellulose replica along. The replica was mounted surface side up on a glass slide. The film was shadowed with chromium or platinum in a vacuum of 10^{-4} Torr. The shadowing angle was varied from 15 to 35° . A thin film of carbon was then deposited, also at 10^{-4} Torr. The specimen was cut with a knife into small squares which were placed on grids, usually copper or nickel (200 mesh). The grids were placed on a piece of filter paper in a flat dish. The filter paper was kept wet with amyl acetate until all the nitrocellulose had dissolved. The carbon replica was then dried.

A Phillips model 300 electron microscope was used in examining the specimens. This instrument has a resolution of $15 \text{ \AA}$. The carbon replica method is good for resolution down to $50 \text{ \AA}$.

D. TiO_2 - SiO_2 Solid State Reactions

A study was made to confirm the solubility of TiO_2 in SiO_2 and also the glass forming ability of the TiO_2 - SiO_2 system as reported by Ricker and Hummel (21). In the solubility study, 0.5 inch diameter wafers were used, while in the glass formation work, the mixed powders were used directly. In both methods, the appropriate amounts of powder were mixed for one hour on a Spex Mixer/Mill. Wafers were prepared by adding polymethylmethacrylate binder to the powder, drying and pressing at 10-15 tsi.

The wafers were placed in a silica dish, presintered to remove binder and then heated to the desired temperature in either a Brew furnace at a pressure of 10^{-4} Torr or a Lindbergh furnace at atmospheric pressure.

The studies in air at atmospheric pressure were carried out in a Glo-bar heated furnace manufactured by the Lindbergh Co. The temperature was measured with a platinum-rhodium thermocouple inserted through an opening in the front of the furnace. Temperature control was $\pm 10^{\circ}\text{C}$. Maximum furnace temperature was 1400°C . After the required time at temperature, the sample was removed and allowed to cool in air. Usually about 0.5 to 1.0 minutes were required to get below red heat.

The studies in vacuum were carried out in a furnace manufactured by the Brew Co. A pressure as low as 5×10^{-5} Torr was obtainable. Maximum furnace temperature was over 2000°C . The specimen temperature was recorded by observation with an optical pyrometer through a quartz window.

The pressed samples were placed in the furnace, the system evacuated and the temperature brought slowly to the desired value. Heat-up time was usually 0.5-1.0 hours. After the required time at temperature, the heat was shut off and the sample allowed to cool in vacuum. Cooling time to below red heat was approximately 5 minutes in vacuum. No interaction was observed between the sample and the sample holder when a solid state reaction occurred. When the wafer melted, bonding to the sample holder was observed.

Since the amount of TiO_2 that is formed if TiSi_2 was oxidized completely to the oxides is 39.9 percent, concentrations at and below this value were studied.

The wafers were analyzed by X-ray and infrared methods. The X-ray analysis was performed on the wafer while the infrared analysis was carried out on the ground powder using the KBr method.

VII. Experimental Results

A. Silicon Oxidation

A number of silicon wafers were oxidized to test the oxidation system and the analytical techniques. These wafers were N-type with the 110 face parallel to the surface. The as-purchased lapped wafers were chemically polished in an etch called C.P. 8 consisting of

75 ml. HNO_3

45 ml. HF

45 ml. Acetic Acid

Etching time was 30 seconds. A mirror-like finish was obtained.

Oxidation was carried out at 1000°C in an atmosphere of 0.2 oxygen and 0.8 argon. X-ray analysis after 100 hours at temperature indicates only the silicon substrate. Absorption peaks in the oxide were obtained at 1080, 805 and 460 cm^{-1} . A faint bump on the broad 1080 peak is observed at 1250 cm^{-1} . When using the reflectance unit, a definite absorption is obtained at 1230 cm^{-1} , while reflection peaks are obtained at 1110, 820 and 465 cm^{-1} . These results correspond quite well with those obtained by Pliskin and Lehman (23) and Murray and Goldsmith (24) for an amorphous SiO_2 film thermally grown on silicon.

The infrared spectrum of a sample oxidized at 800°C is similar to that obtained at 1000°C . Since the oxide thickness is considerably lower at this temperature, it would be expected that the Si-O absorption would be shifted to a lower frequency. This is what is observed.

Rate data were obtained for silicon oxidized at 1000°C in an atmosphere with an oxygen partial pressure of 0.20. When the square of the weight gain is plotted against time, a straight line passing through

the origin is obtained. The average value of the parabolic rate constant is $1.19 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2\text{/hr.} \pm 0.17 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2\text{/hr.}$ Deal and Grove (29) report a value of $1.57 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2\text{/hr.}$ for the parabolic rate constant at 1000°C . This is quite good agreement considering that great care was not taken in preparing the surfaces. These results indicate that the experimental procedure and equipment are suitable for obtaining oxidation rate data for the disilicides.

A few data points were also obtained for silicon oxidized at 800 and 600°C . At 800°C , a weight gain of only 120 μg is observed after 50 hours of oxidation. At this time, the sample exhibits a bright purple interference color. Insufficient data were taken to comment on the oxidation mechanism.

A wafer oxidized at 600°C in a oxygen atmosphere shows a weight gain of only 30 μg after 300 hours. No meaningful rate data could be obtained at this low level. No interference colors are observed with the sample.

B. TiSi_2 Oxidation

1. Sample Quality

In order to obtain reliable oxidation rate data, it is necessary that the sample surface be uniformly clean, both chemically and physically. In a system of the type studied here, it is difficult to prepare wafers that contain only a single compound. As indicated by the phase diagram shown earlier in Figure 2, there are three compounds in the titanium-silicon system. When preparing either of these materials, a second phase is bound to be present. For example, if a slight excess of silicon is present when preparing wafers of TiSi_2 , a silicon phase is observed. At the high sintering temperatures used, a loss of one of the elements

occurs, in this case silicon. If, therefore, stoichiometric amounts are used, a deficiency of silicon will be observed resulting in the presence of a lower silicide phase.

Since it is also difficult to obtain densities that are equal to the theoretical values using the powder metallurgy technique, physical defects are also to be expected.

Considerable effort was spent developing the technique for preparing the TiSi_2 wafers. The method involves sintering the pressed pellet at 1380-1400°C in a vacuum of 5×10^{-5} Torr. Samples made from CERAC TiSi_2 have densities of 93-96 percent of theory, as determined by water displacement. When the sample volume is determined by direct measurement with a micrometer, these percentages are lower by 1-2 percent. This difference is probably due to the presence of pores in the sample surface.

As the sintering temperature is decreased below 1380°C, the sample density decreases. At temperatures above 1400°C, the samples warp badly and in some cases adhere to the alumina dish in which they are supported.

Typical micrographs of an etched TiSi_2 wafer prepared from CERAC powder are shown in Figures 3 and 4. The TiSi_2 grain size is approximately 50-70 microns. In addition to the TiSi_2 , there is a second phase which collects at the intersection of three silicide grains. X-ray analysis of the surface shows TiSi_2 and a small amount of silicon. The silicon is apparently the second phase that is observed. There are also a number of holes in the sample surface as indicated by the black area in Figure 4. These appear to be primarily in the silicon phase and may result from pulling out during polishing. Under polarized light, the TiSi_2 grains show up as two distinct shades, possibly indicat-



Figure 3. TiSi₂ Wafer Fabricated from CERAC Powder, 125 X.



Figure 4. TiSi₂ Wafer Fabricated from CERAC Powder, 320 X.

ing two preferred orientations.

An electron micrograph of the surface, Figure 5, shows small scratches and a number of pits possibly due to the etch. The TiSi_2 phase is considerably more pitted than the silicon phase in the center of the Figure. There also appears to be a groove between the silicon and the silicide phase.

The large grain size and apparent preferred orientation result in differences between the observed and ASTM standard X-ray intensities. This is shown by some typical data in Table 6. Of greater significance is the fact that the observed angle positions are lower than those given by the ASTM. X-ray patterns obtained with the CERAC powder give similar results. The lower angle indicates that the interatomic lattice distances are larger than those given by the ASTM data. This may be due to silicon interstitially dissolved in TiSi_2 .

The infrared spectrum of an etched TiSi_2 wafer was determined using the microspecular reflectance attachment. An extremely weak absorption was observed at 1040 cm^{-1} . This probably indicates that even after etching an extremely thin film of SiO_2 is present.

The excess silicon (0.68%) was removed from the CERAC TiSi_2 powder by treating with a 10% NaOH solution at 40°C . A typical micrograph of a wafer prepared from NaOH-washed TiSi_2 is shown in Figure 6. The silicon phase observed with the unwashed CERAC TiSi_2 has disappeared while another smaller, more circular phase is present. X-ray analysis shows only TiSi_2 , no silicon or lower titanium silicides are indicated. In several samples, Ti_5Si_3 was indicated. The interatomic distances for the TiSi_2 were again greater than the ASTM values. They were, how-

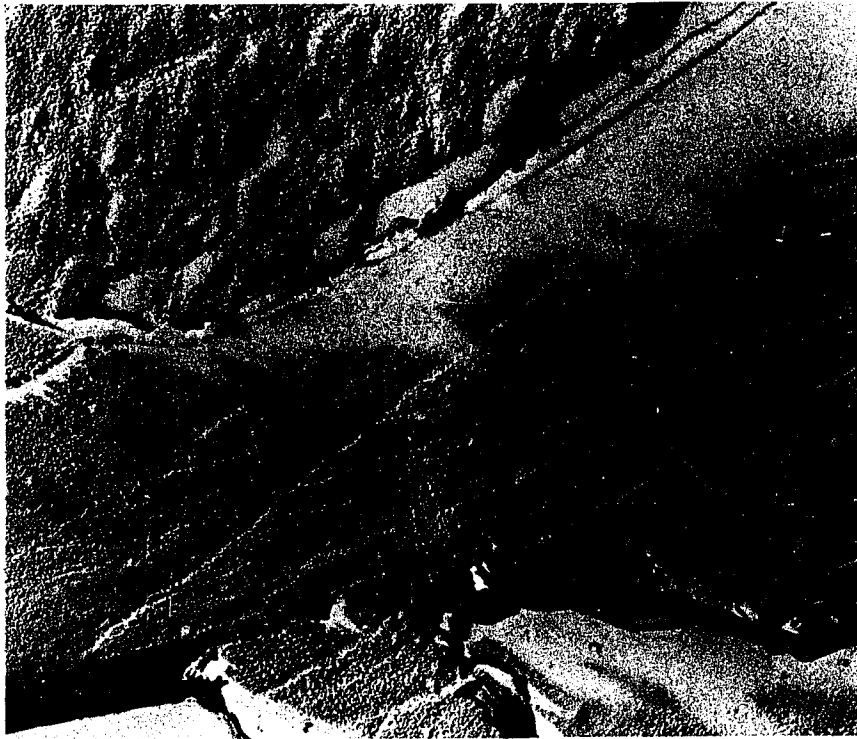


Figure 5. Electron Micrograph of Unoxidized
CERAC TiSi₂ Wafer, 12,000 X.

Table 6

Comparison of Observed and ASTM X-ray

Data for TiSi_2

<u>Experimental</u>		<u>ASTM</u>		<u>Identification (hkl)</u>
<u>2θ</u>	<u>I/I_1</u>	<u>2θ</u>	<u>I/I_1</u>	
23.85	5	-	-	*
28.45	100	28.42	100	Si(111)
30.02	5	-	-	*
39.12	100	39.30	100	$\text{TiSi}_2(311)$
42.30	3	42.40	70	$\text{TiSi}_2(004)$
43.23	53	43.46	90	$\text{TiSi}_2(022)$
47.35	75	47.30	60	Si(220)
49.78	67	50.08	90	$\text{TiSi}_2(313)$
68.70	11	69.00	70	$\text{TiSi}_2(331)$
71.96	13	72.02	90	$\text{TiSi}_2(602)$

*These two peaks were found in all the TiSi_2 wafers prepared.



Figure 6. TiSi₂ Wafer Fabricated from NaOH-Washed CERAC Powder, 125 X.

ever, not as great as those observed with the unwashed CERAC TiSi_2 .

This is consistent with the idea of interstitial silicon since the caustic wash would be expected not only to remove the silicon found as a separate phase, but also to some extent remove some of the dissolved silicon.

A higher magnification of this second phase shows another phase between the disilicide and the second phase. If the second phase is Ti_5Si_3 , the small intermediate layer would logically be TiSi . There are fewer and smaller holes in these specimens than in those made with the unwashed CERAC TiSi_2 .

Samples prepared from NaOH-washed CERAC TiSi_2 had densities, as determined by water displacement, of 95-98 percent of the theoretical values. Densities obtained by direct measurement with a micrometer were lower, but not as much as with wafers made from the unwashed CERAC TiSi_2 .

Samples were also prepared from TiSi_2 made by direct reaction of titanium and silicon. To the unaided eye, these appear similar to the samples made from caustic-washed CERAC TiSi_2 . In many samples, there appears to be a second phase which is similar to that observed with the CERAC TiSi_2 where excess silicon is present. X-ray analysis, however, shows only TiSi_2 . The amount of the second phase is considerably lower than that in the unwashed CERAC samples and, as such, it is possible that the X-ray method is not sufficiently sensitive. As in earlier samples, the holes appear to be in either this second phase or at the junction of three grains.

2. Character of the Oxide Film

Wafers of TiSi_2 were oxidized at temperatures of 300-1350°C in

oxygen-argon atmospheres where the oxygen partial pressure was varied from 0.2 to 1.0. Below 300°C, negligible oxidation occurs.

At 300°C, where the weight gain is almost negligible, no visible continuous oxide is observed. A few, very small, multicolored crystalline areas are present on the sample surface when viewed at a magnification of 400X. X-ray analysis shows only the TiSi_2 substrate which does not change during the course of oxidation. Under polarized light, the entire field is dark. The few crystalline-appearing areas observed may be due to oxides of impurities in the silicide.

At 600°C and an oxygen partial pressure of 0.2, a multicolored, transparent oxide film is formed. In the initial stage of oxidation, there are usually two or three interference colors that are observed from the oxide when viewed by the unaided eye. On microscopic examination within each color region, it is found that this overall color is a blend of several color areas. Each of these color areas corresponds roughly in size and shape to the TiSi_2 grain structure. When a separate silicon phase is present in the substrate, the oxide formed on it exhibits a different interference color. This color is usually the same on all silicon areas throughout the sample.

As the time of oxidation increases, the colors observed on the TiSi_2 grains show gradual changes. The color displayed by the oxide on the silicon phase remains a light tan to pale brown throughout the course of a run. Based on interference charts developed for the oxide formed on silicon (41), the light tan color indicates an oxide film thickness of about 500 Å.

Examination of the oxide film with a light microscope reveals no

crystalline regions after 300 hours of oxidation. X-ray analysis indicates only the TiSi_2 substrate with interatomic distances that are constant through the oxidation period. Observation under polarized light shows lighter colored areas within the holes in the sample surface.

At 800 hours of oxidation, microscopic examination indicates a number of small, yellow crystalline islands. These are found near the holes originally observed in the TiSi_2 surface. X-ray analysis indicates only TiSi_2 .

An electron micrograph of the oxide formed on TiSi_2 after 200 hours of oxidation at 600°C is shown in Figure 7. The oxide has the same topography as the unoxidized TiSi_2 shown earlier in Figure 5. No difference can be observed between the oxide growing on the silicon phase, the upper right side, and on that growing on the TiSi_2 phase. Of particular significance is the lack of amorphous phase separation or crystallization in the oxide on the TiSi_2 .

At 800°C , a significant change occurs in the structure of the growing oxide film. In the initial stage of oxidation, metallographic and X-ray examination indicate an amorphous film similar to that obtained at 600°C . The interference color is more uniform over the surface compared to 600°C where the thickness varies with grain orientation. After three hours, however, small clumps of crystalline TiO_2 are observed. These clumps are approximately 50 microns in diameter. A typical micrograph is shown in Figure 8. X-ray diffraction indicates that the TiO_2 is in the rutile form. The crystalline areas are generally found at the phase boundary of the silicon and TiSi_2 phases. This is also the region where most of the holes in the surface are observed. As the reaction

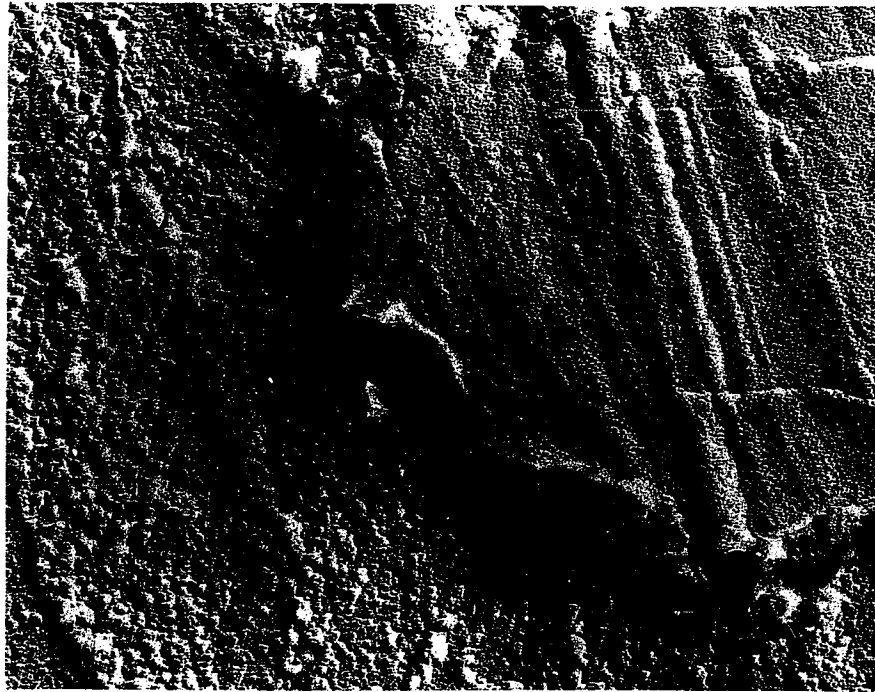


Figure 7. Electron Micrograph of Oxide Formed on TiSi_2 Oxidized at 600°C , 42,000 X.



Figure 8. Micrograph of Oxide Formed on TiSi_2
Oxidized at 800°C , 320 X.

time increases, more clumps are observed while those formed earlier increase slightly in diameter. Also of interest is the fact that the TiO_2 is growing up and out of the amorphous silica film. This is easily observed with a light microscope at 400X magnification. Under polarized light, the crystalline areas appear bright yellow, while the surrounding amorphous region is dark.

At 1000°C, the oxide film is similar to that obtained at 800°C. X-ray and metallographic studies indicate an amorphous matrix with crystalline islands of TiO_2 (rutile). The crystallization occurs after about one hour at reaction temperature compared to the three to seven hours observed at 800°C. With wafers made from "homemade" TiSi_2 , the observable crystallization occurred at a longer time, approximately ten hours. In these samples, there is a negligible silicon phase. Most of the crystallization occurs at the silicide grain boundaries. The TiO_2 clumps are more numerous and larger in size than those formed at 800°C for comparable oxidation times.

An electron micrograph of the oxide formed on TiSi_2 after 100 hours of oxidation at 1000°C is shown in Figure 9. The sample was etched for two minutes in "P" etch prior to preparing the replica. As at 600°C, the amorphous part of the film follows the contour of the TiSi_2 substrate. No amorphous phase separation is observed. A crystalline clump of TiO_2 is indicated in the upper right hand part of Figure 9. This structure, formed at the boundary of the TiSi_2 and silicon phases is typical of that found throughout the sample. Other considerably smaller islands of TiO_2 are found within the TiSi_2



Figure 9. Electron Micrograph of Oxide Formed on TiSi_2 Oxidized at 1000°C , 7500 X.

phase. Examination of the sample after four additional two-minute etch periods indicated the same structure.

Little information was obtained by examining a cross-section of the oxide with a light microscope since the oxide film is quite thin (1-2 microns). A narrow white band is all that could be observed. An attempt was made to prepare a replica of the cross-section for examination with the electron microscope. This was unsuccessful due to tearing of the replica in the region of the oxide-plastic boundary when removing the nitrocellulose film.

At 1200°C, the characteristic amorphous silica film with crystalline TiO_2 (rutile) islands growing out and above the silica is observed. Crystallization of the TiO_2 occurs within 0.5 hours at temperature. These TiO_2 islands also grow laterally and vertically with time. X-ray analysis indicates that α -cristobalite is also present at 0.5 hours. Many small multi-colored crystalline-like areas also appear in the film after about 30 hours. This is probably the α -cristobalite observed in the X-ray.

A cross-section of the oxide formed on TiSi_2 after 100 hours at 1200°C is shown in Figure 10. This micrograph was made using polarized light with a magnification of 1600X. In this particular light, the white silica layer is easily observed. The two darker colored regions within the top of the film appear to be TiO_2 . At a number of places where holes appear in the surface, the TiO_2 growth is quite pronounced. It extends considerably above the silica film and appears to penetrate to the bottom of the hole. There is also a small amount of lateral growth on top of the amorphous silica part of the film.



Figure 10. Cross-section of Oxide Formed on TiSi_2
Oxidized at 1200°C for 100 Hours, 1600 X.

At 1350°C, the character of the oxide film is considerably changed. No interference colors are observed, the sample is dark grey with a glassy oxide which is thicker in the center of the sample. The wafer is distorted slightly, being concave up. A micrograph of the surface oxide after 83 hours at 1350°C is shown in Figure 11. The white areas have the appearance of crystalline planes formed during solidification of a liquid. The usual X-ray and infrared technique could not be used for analysis due to the distortion of the sample. Because of this warping, the practical upper use limit for titanium disilicide is approximately 1300°C.

In order to characterize the amorphous region of the oxide film, the infrared spectra of a number of samples were obtained. Some typical results are shown in Figure 12 and summarized in Table 7. More detailed data are given in Appendix A. The results shown in Figure 12 and Table 7 were obtained at extended oxidation times where the positions of the absorption maxima have stabilized.

The infrared spectrum of the oxide formed at 300°C is indicated in Figure 12(a). This result was obtained using 5X ordinate expansion. As indicated, there is faint evidence of a very thin silica film. Little can be deduced about the structure from the broad, low intensity absorptions.

The spectrum obtained at 600°C is given in Figure 12(b). The absorption peak normally observed at 1250 cm^{-1} has shifted to 1150 cm^{-1} and has become quite broad. The Si-O vibration at 1100 cm^{-1} has moved to 1040 cm^{-1} while the Si-O-Si bond bending at 460 cm^{-1} has shifted to 435 cm^{-1} . These shifts to lower frequencies are indicative of low density or impurities in the film. The broadness of the peaks also indicates considerable variation in the bonds.



Figure 11. Micrograph of Oxide Formed on TiSi_2
Oxidized at 1350°C , 125 X.

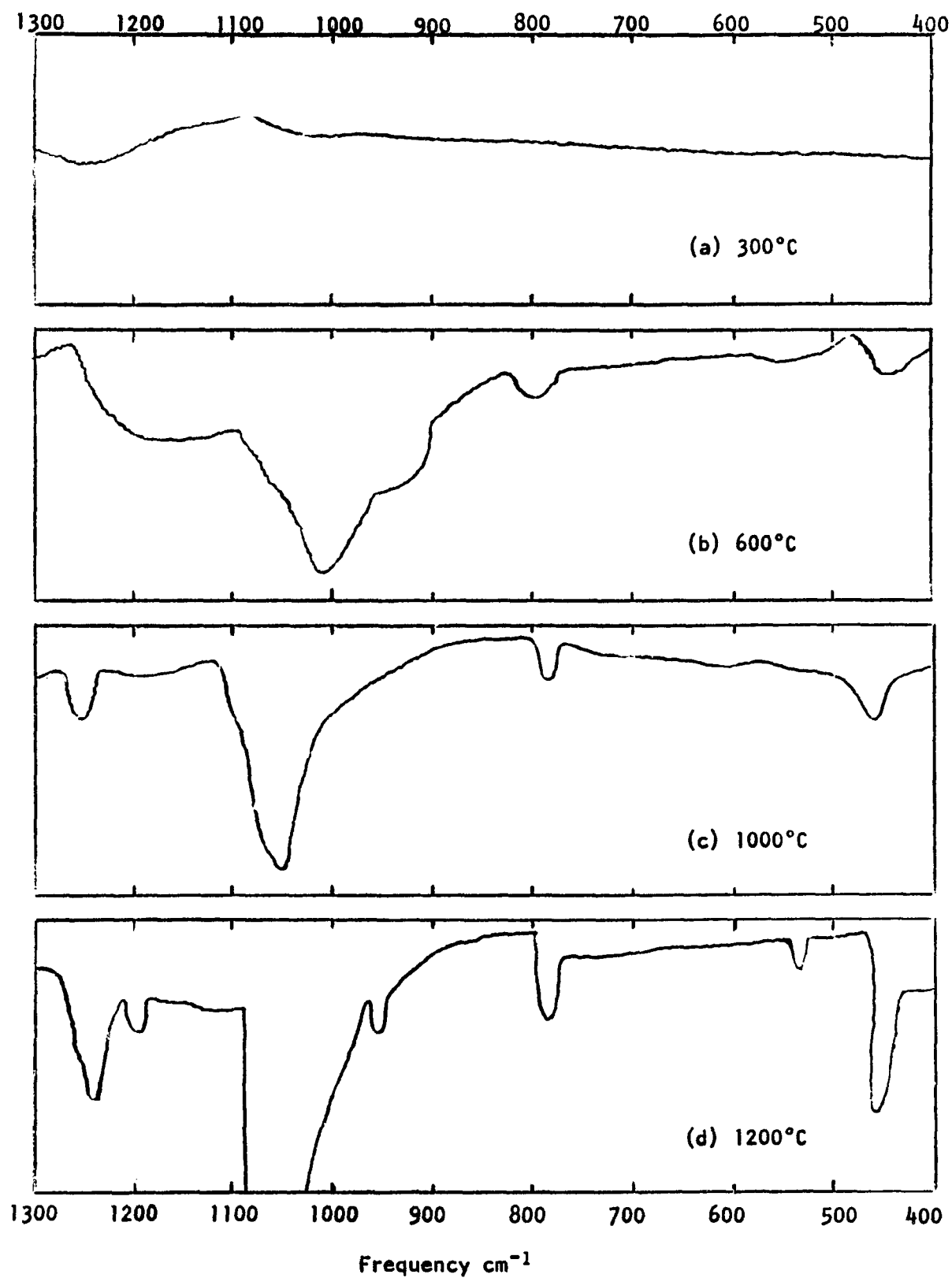


Figure 12. Infrared Spectra of Oxide Grown on TiSi_2 at 300-1200°C

Table 7

Summary of the Infrared Results of the Oxide
on TiSi_2 Oxidized at 300 - 1200°C

Oxidation Temp., °C	Absorption Maxima, cm^{-1}						
300	1250(VW)	-	1040(VW)	-	-	-	-
600	1200(B)	-	1040	930(B)	800	-	440
800	1255	-	1060	-	780	-	X
1000	1254	-	1065	-	780	-	X
1200	1254	(1195)	1058	950	785	535	465
Amorphous SiO_2 Film(23)	-	-	1100	-	800	-	465

(VW) - Very weak

(B) - Broad peak

X - Region not investigated

In addition to the shifts in the normal silica vibrations, a significant broad absorption is observed at 930 cm^{-1} . Bulk $\text{TiO}_2\text{-SiO}_2$ studies (see section VII D) indicate that this is due to a Ti-O-Si vibration. The strength of this peak indicates a considerable amount of this structure. As at 300°C , it was necessary to use 5X ordinate expansion to locate the position of maximum absorption.

The infrared spectrum was recorded during the course of a 187 hour oxidation run at 600°C . The spectra at 54 and 187 hours of oxidation appear to be identical except for the 940 cm^{-1} absorption which is slightly stronger at the longer time. This indicates that the character of the oxide is not undergoing any appreciable change during this oxidation period.

At 800 and 1000°C , the spectrum is that of silica with the major Si-O vibration at 1060 cm^{-1} . No absorption is observed at 930 cm^{-1} . The increase in frequency from 1040 to 1060 cm^{-1} when the temperature is increased from 600 to 800°C indicates a more dense or higher purity silica film at the higher temperature. The absorption maxima for high purity SiO_2 on silicon is $1090\text{--}1100\text{ cm}^{-1}$ (23). The amorphous silica matrix formed at 1000°C on TiSi_2 then is not as pure or dense as that formed on silicon when it is oxidized. The lack of an absorption at 930 cm^{-1} indicates a lack of Ti-O-Si bonding in the amorphous region. This is not surprising since TiO_2 has crystallized into small clumps.

The shift in the position of the absorption maxima and the appearance of a new peak are well known in the study of bulk glasses. Simon and McMahon (43) indicated a shift to a lower frequency of the 1100 cm^{-1} Si-O vibration and also the formation of a new peak at 930 cm^{-1} as Na_2O was added to SiO_2 . For a more detailed discussion of this result, see

Appendix A.

The spectrum at 1200°C, Figure 12(d), shows silica with additional vibrations at 1190, 950 and 535 cm^{-1} . The 1195 and 950 cm^{-1} peaks appear to be related to the major vibrations at 1245 and 1058 cm^{-1} respectively. The peaks are very much sharper than at lower temperatures indicating a more ordered structure. These three peaks may be additional Si-O stretching modes resulting from the more ordered structure. The fact that the major Si-O vibration is found at 1060 cm^{-1} , which is 40 cm^{-1} less than where pure SiO_2 would be observed, indicates that while the structure is becoming more ordered, the impurity in the network is still present.

The infrared spectra in the initial oxidation period are different from that observed at longer times. This is indicated by the data in Table 8. Up to four hours of oxidation at 1000°C, only the 1250 and 1050 cm^{-1} vibrations are observed. The position of the 1250 cm^{-1} peak is fairly constant during this initial period, while the Si-O stretching frequency increases from 1000 cm^{-1} at 0.5 hours to 1035 at four hours. In each spectrum, a weak absorption is also observed at 900-950 cm^{-1} . For reaction times greater than about 10 hours, the positions of the absorption maxima appear to be relatively stable.

Murray and Goldsmith (24) and Sato and Shibata (25) indicate an increase in the position of the reflection maxima of the Si-O vibration of 50 cm^{-1} when the SiO_2 thickness on silicon is increased from 0.1 to 1.0 microns. This shift has been attributed (25) to the presence of free silicon bonds in the silica as the oxide-air interface is approached. The shift could also be due to an increase in oxide density as the structure assumes its more stable form.

Table 8

Effect of Oxidation Time at 1000°C on
Infrared Absorption Maxima Positions

<u>Spectrum</u>	<u>Run</u>	<u>Oxidation Time, Hrs</u>	<u>Wt. Gain, mg/cm²</u>	<u>Absorption Maxima, cm⁻¹</u>			
25	8	0.5	0.0722	1255	1000		
26	8	1.0	0.1045	1252	1020		
27	8	2.25	0.1455	1250	1030		
30	75	1.0	0.0140	1250	1020		
31	75	4	0.0258	1255	1035		
32	75	100.5	0.123	1255	1050	780	460

3. Rate Data

The variables that were considered in the rate study were: surface quality, gas flow rate, temperature and oxygen partial pressure. The quality of the surface was considered qualitatively while the other variables could be investigated quantitatively.

In the initial phase of the study, the effect of gas flow rate was considered. Several wafers of TiSi_2 were oxidized at 600 - 1000°C in an atmosphere with an oxygen partial pressure of 0.20. The gas flow rate was varied from 0 to 200 cc/min. Within experimental error, no effect is observed with changing gas rates. These results indicate that mass-transfer through the gas phase is rapid compared to the other steps in the reaction. This same result was obtained by Deal and Grove (29) in their studies of the oxidation of silicon. Since most of the later experiments were carried out at conditions where the oxidation rate would be lower, the effect of gas flow rate could readily be neglected. In all the later studies, the gas flow rate was fixed at 200 cc/min. in order to insure a uniform gas composition in the reactor.

A single sample of TiSi_2 prepared from CERAC powder was oxidized at 300°C in order to establish the lower level of observable oxidation. After 20 hours at temperature, a total weight gain of 25 μg is observed. After 320 hours, the weight gain increases to 112 μg . A summary of the data obtained at 300°C is shown by the lower curve in Figure 16.

Based on the analysis of the oxide film described earlier, there appears to be two reactions occurring at 300°C. One is the formation of a very thin amorphous SiO_2 film and the other a localized reaction, possibly of impurities. Assuming an oxide density of 2.2 gms/cm³, the

observed weight gain corresponds to a film 1270 Å thick. Since TiO_2 may be dissolved in the film, the density could be considerably greater. The observed interference color indicates a film less than 500 Å thick if the color charts developed for silicon oxidation are used (41). If TiO_2 were dissolved in the film, the refractive index would be greater and the film would be thinner than what is indicated by the color charts.

These results indicate that the weight gain due to the point reaction is significant. Since the weight gain associated with this reaction cannot be determined, it is not possible to make a quantitative evaluation of the thin film formation.

Since the sample quality was not good enough, no further studies were made to evaluate the mechanism at 300°C.

Typical weight gain data for TiSi_2 oxidized at 600°C are shown in Figure 13. The most noticeable characteristic of the data at this temperature is the sharp break in the curve at about 9 hours. The value of n in the expression $X^n = kt$ for times less than 9 hours is 2-3, while after the break, values of 8-10 are observed.

When these data are replotted as the square of the weight gain versus time, the curves shown in Figure 14 are obtained. If this were a simple diffusion controlled process, a straight line would have been obtained. While this is not the case, the slope does appear to be approaching a constant value. If it is assumed that the slope is constant after 150 hours, a parabolic rate constant equal to $85 \times 10^{-7} (\text{mg}/\text{cm}^2)^2/\text{hr}$ is obtained.

At 600°C, the oxygen partial pressure was varied from 0.2 to 1.0 atmospheres. Within experimental error, no effect is observed when the

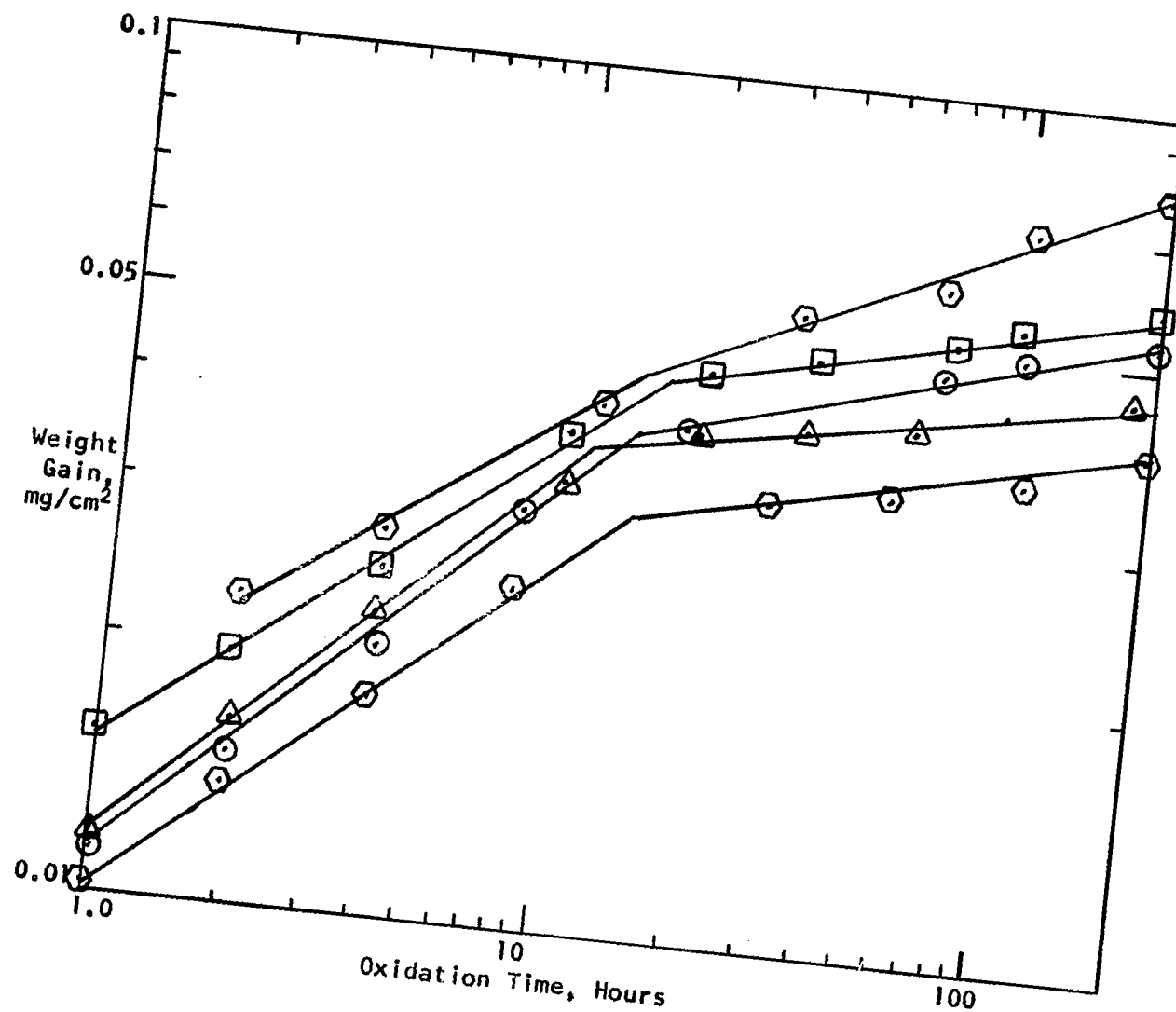


Figure 13. Weight Gain Data for TiSi_2 Oxidized at 600°C

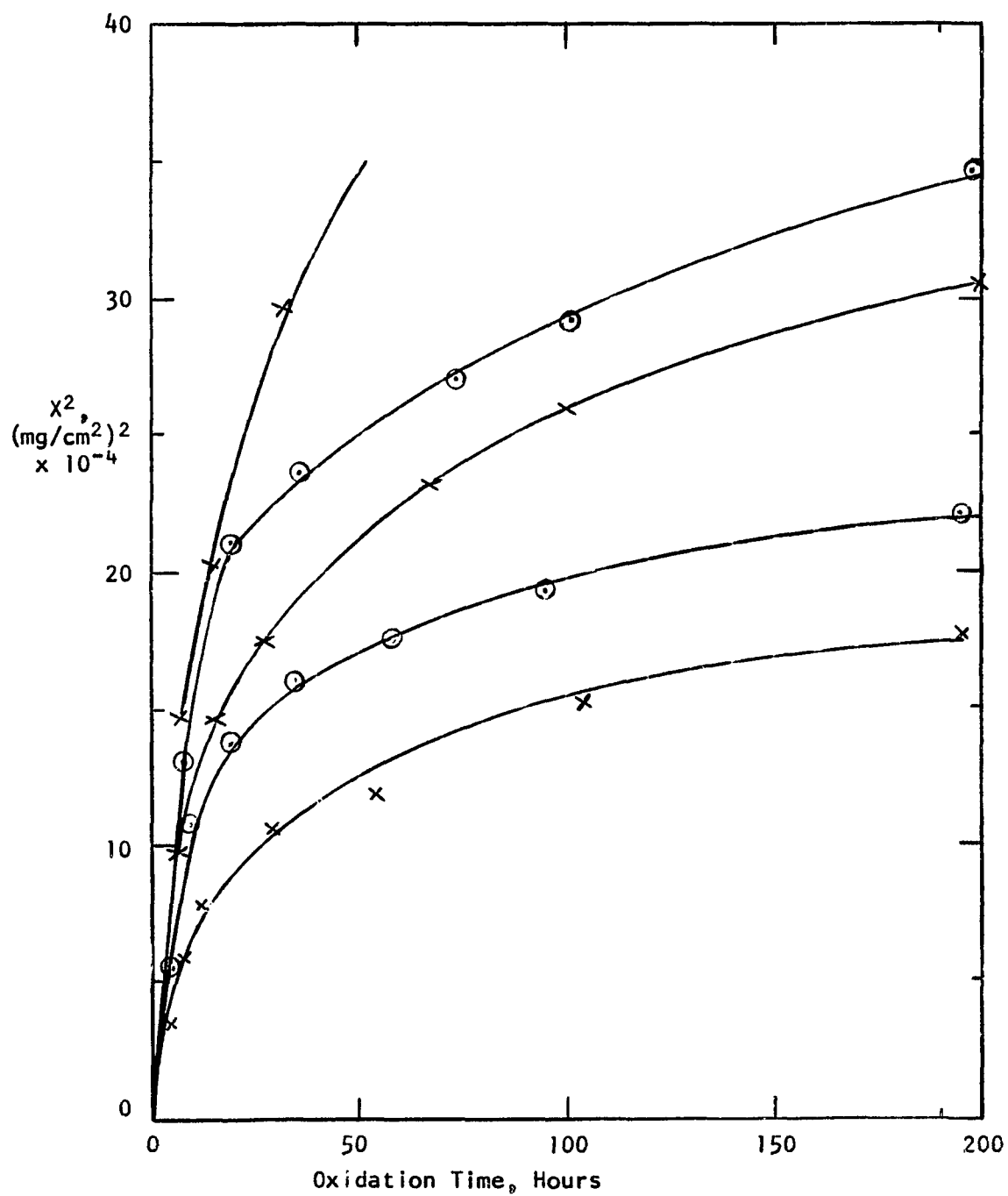


Figure 14. X^2 versus t for TiSi_2 Oxidized at 600°C

oxygen pressure is varied in this range.

The type of powder used, whether straight CERAC TiSi_2 , NaOH-washed TiSi_2 or homemade TiSi_2 does not appear to affect the rate. In addition, varying the sample density of CERAC TiSi_2 wafers from 91.5 to 95.2 percent of theory does not affect the rate of oxidation. While no effect was observed due to preparation methods, the variation in weight gain shown in Figure 13 is probably due to differences in surface quality.

At 800°C, results similar to those obtained at 600°C are observed. In this case, the break in the weight gain curve occurs at about 6 hours compared to the 9 hours obtained at 600°C. Within experimental error, the magnitude of the observed weight gain for the first 50 hours is the same as that observed at 600°C. Beyond 50 hours, the weight gain at 800°C becomes greater.

A plot of X^2 versus time for the 800°C data shows curves similar to those obtained at 600°C (see Appendix C). No straight line regions are observed. If a straight line is assumed after 100 hours, a parabolic rate constant equal to $0.26 \times 10^{-4} (\text{mg}/\text{cm}^2)^2/\text{hr}$ is obtained. No change in rate is observed when the oxygen pressure is changed from 0.2 to 1.0.

As indicated earlier, the surface quality depended on the history of the TiSi_2 powder and its subsequent treatment. When oxidized at 1000°C, a significant difference in rate is observed depending on the powder used in the sample preparation.

Samples prepared with either CERAC TiSi_2 or NaOH-washed CERAC powder give similar rate data. Both sample types give higher weight gains due to imperfections in the surface. In the case of the samples

prepared from NaOH-washed CERAC powder, there is a small amount of a second phase, Ti_5Si_3 . This lower silicide oxidizes at a much faster rate than does $TiSi_2$. The samples prepared from unwashed CERAC powder have a greater number of holes. Oxidation would be expected to occur at a faster rate at these high energy sites. The presence of small amounts of Ti_5Si_3 appears to have an effect similar to the holes, i.e., to increase the crystallization of TiO_2 resulting in larger local weight gains. As indicated earlier, the amorphous region over the $TiSi_2$ in either sample is the same.

The average result obtained at $1000^\circ C$ with wafers made from homemade $TiSi_2$ showed an interesting contrast. In some cases, no difference in rate could be observed between these samples and samples made from the CERAC powder. In a few runs, lower initial weight gains and definite parabolic behavior in the entire region are indicated. This result is shown in Figure 15 where X^2 is plotted against t . In each case, extrapolation through the origin is observed. A summary of the rate constants obtained is given in Table 9. A value of $3.52 \times 10^{-4} (mg/cm^2)^2/hr$ is obtained from the slope for the parabolic rate constant.

When the oxygen pressure is increased from 0.2 to 1.0, there appears to be an increase in the oxidation rate. Parabolic behavior with a rate constant equal to $4.06 \times 10^{-4} (mg/cm^2)^2/hr$ is obtained. The samples for which the results were obtained appear to have better surfaces, i.e., fewer holes and no lower silicides.

The oxidation rate data at $1000^\circ C$ obtained with samples prepared from either unwashed CERAC powder or NaOH-washed CERAC powder showed two major differences when compared to the homemade $TiSi_2$ data.

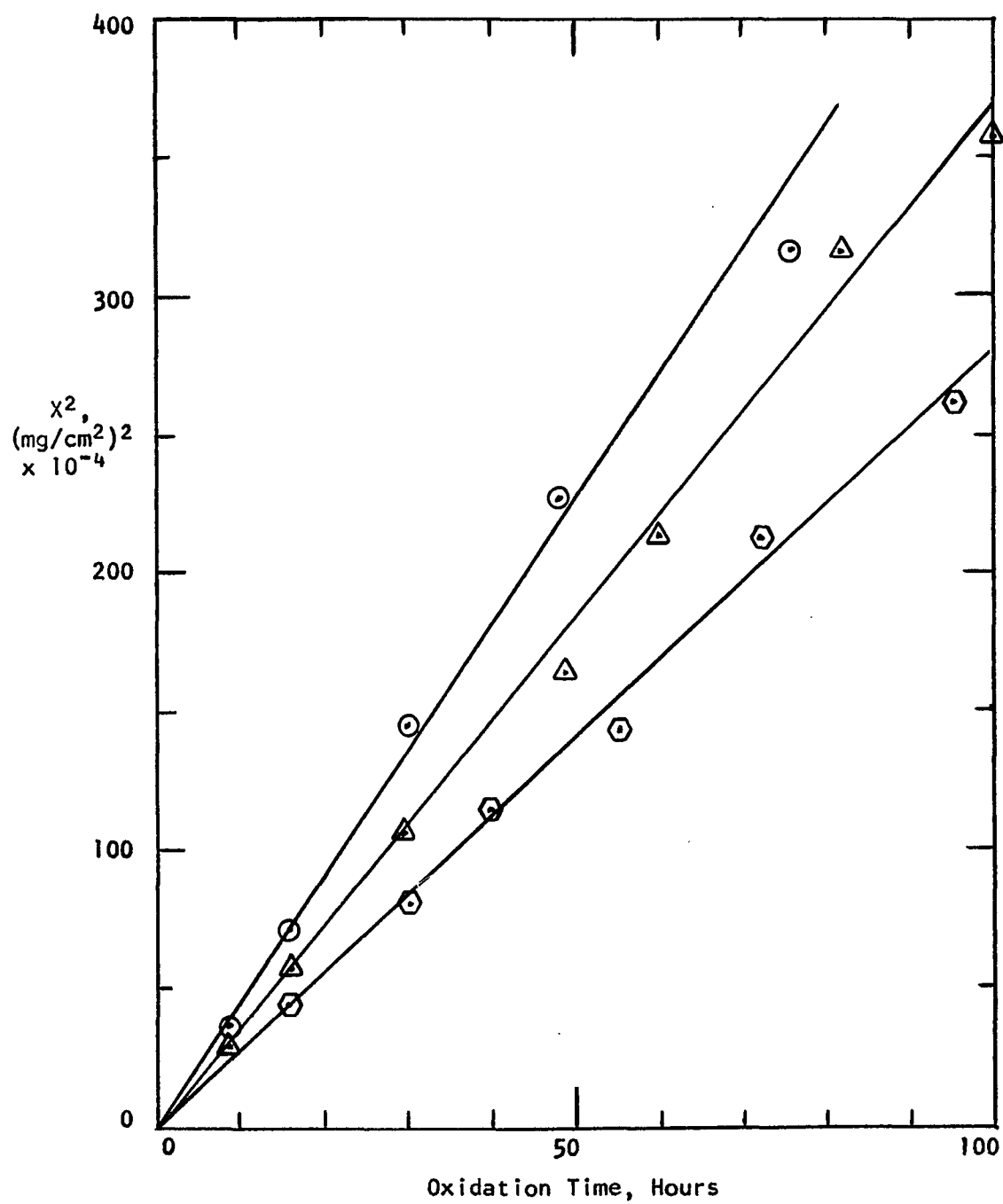


Figure 15. X^2 versus t for TiSi_2 Oxidized at 1000°C

Table 9

Parabolic Rate Constants Obtained by Oxidizing
Homemade TiSi_2 at 1000°C

<u>Run Number</u>	<u>k_p (mg/cm^2)²/hr</u>	<u>Standard Deviation</u>
75	4.57×10^{-4}	0.09×10^{-4}
78	2.80×10^{-4}	0.04×10^{-4}
80	3.11×10^{-4}	0.03×10^{-4}
81	3.60×10^{-4}	0.05×10^{-4}

Average value of $k_p = 3.52 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2/\text{hr}$

Average deviation
within runs $= 0.05 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2/\text{hr}$

Standard deviation
between runs $= 0.77 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2/\text{hr}$

As at 600 and 800°C, a break is observed when the log of the weight gain is plotted against the log of the time. At 1000°C, however, the break is observed at 1 - 3 hours compared to 6 hours at 800°C and 9 hours at 600°C.

When the 1000°C data is plotted as X^2 versus t , a straight line is obtained for times greater than 5 hours. At times less than 5 hours, the values of X^2 are considerably below the straight line. In addition, the lines do not extrapolate through the origin, rather through positive values on the ordinate.

Also of significance is the total weight gain of the CERAC samples compared to the homemade. Higher weight gains are observed for samples made from the CERAC powder.

The kinetic data obtained at 1200 and 1300°C are similar to those obtained at 1000°C. Using wafers made from either untreated or NaOH-washed CERAC TiSi_2 gives a parabolic expression of the form $X^2 = kt + c$, where c is a positive number. When homemade TiSi_2 is used, parabolic behavior with $c = 0$ is observed. The average value for k_p is $8.72 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2\text{/hr}$ with a standard deviation of $1.48 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2\text{/hr}$.

When the oxygen partial pressure is increased to 1.0 at 1200°C, the average value of k_p obtained is $10.03 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2\text{/hr}$ with a standard deviation of $0.94 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2\text{/hr}$. This result indicates that there is a slight increase in the parabolic rate constant as the oxygen pressure is increased from 0.2 to 1.0 atmospheres. Data obtained with the CERAC TiSi_2 also show a slight increase in the oxidation rate when the oxygen pressure is increased from 0.2 to 1.0.

At 1300°C and an oxygen partial pressure of 0.2 atm., a value of $17.4 \times 10^{-4} \text{ (mg/cm}^2\text{)}^2\text{/hr}$ is obtained for the parabolic rate constant. Only two short runs were made at this temperature since the vitreosil sample holder started to devitrify. Small crystals chipped from the holder, some of which landed on the specimen being oxidized. At short times, these could be brushed from the surface prior to weighing. At long times, however, these specks became attached to the growing oxide. Further studies at this temperature will require a different support material.

A summary of what appears to be the best rate data for the oxidation of TiSi_2 is shown in Figure 16. At temperatures of 600 and 800°C, the data are for all samples investigated. At 1000 - 1300°C, the results are given for samples made from homemade TiSi_2 powder.

An Arrhenius plot of the data at 1000 - 1300°C is shown in Figure 17. A straight line is obtained. The activation energy calculated from the slope is 21.3 kcal.

C. Other Silicides Studied

1. TiSi

In the titanium-silicon phase diagram shown earlier, there are two compounds in addition to TiSi_2 . These are TiSi and Ti_5Si_3 . Wafers of these lower silicides were prepared using the same technique that was used in preparing the disilicide.

Since TiSi is not commercially available, it was prepared by direct reaction of titanium and silicon at 1075°C and 10^{-4} Torr. A silicon excess of 0.5% of the stoichiometric value was used. The reaction product was ground, mixed with binder and pressed into 1 inch

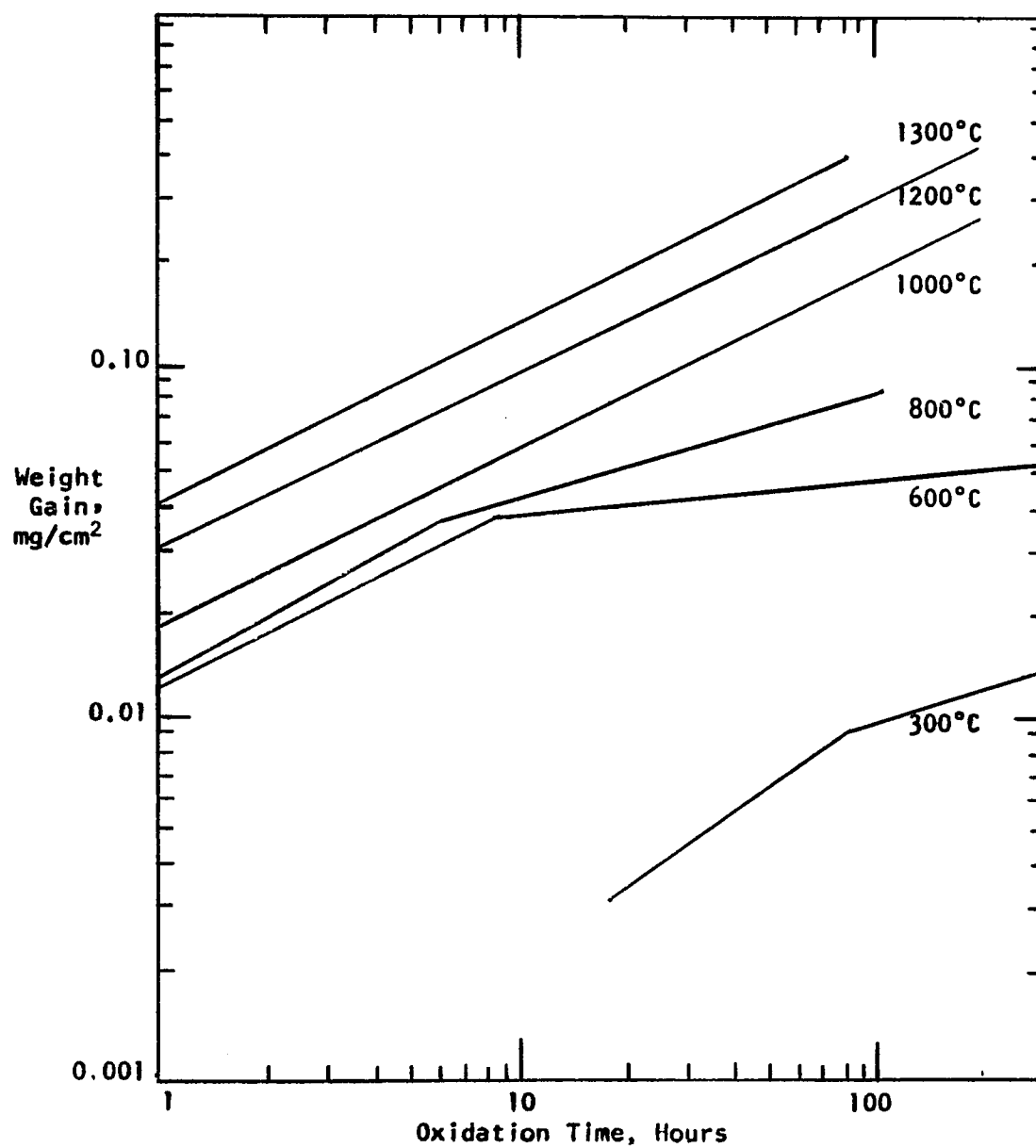


Figure 16. Summary of TiSi_2 Oxidation Rate Data: 300-1300°C

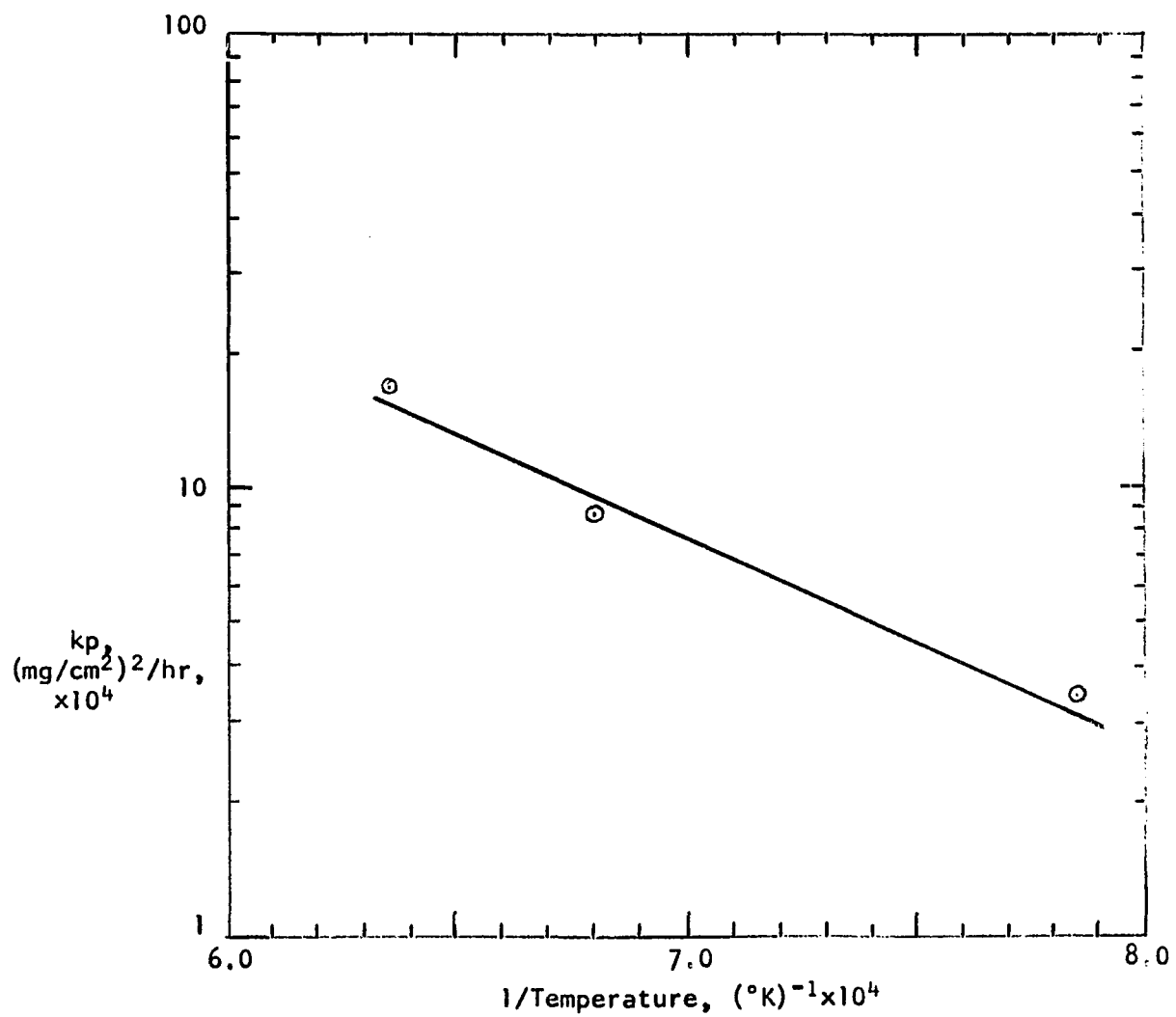


Figure 17. Arrhenius Plot of TiSi_2 Oxidation Data

diameter disks. Sintering was achieved at 1350°C and 10^{-4} Torr.

Samples fabricated in this way have densities, as determined by water displacement, of 90-97 percent of the theoretical values. As is the case for TiSi_2 , the density by direct measurement is 2 to 3 percent lower. The polished surfaces appear mirror-like.

Typical micrographs of two etched samples prepared using this technique are shown in Figures 18 and 19. These data indicate considerable variation in surface quality. The sample with few holes, Figure 18, has a density of 96 percent of theory. In addition to the holes, there is also a fair amount of a second phase. X-ray analysis indicates TiSi with a small amount of TiSi_2 . Since it is not possible to prepare a sample of only TiSi , it is desirable to have TiSi_2 as the second phase rather than Ti_5Si_3 . If TiSi forms a protective silica film on oxidation, TiSi_2 , since it contains more silicon, would also form one, while Ti_5Si_3 would be more likely to form a titania rich oxide which might disrupt the silica film.

The X-ray diffraction results show that the interatomic spacings in the TiSi are greater than those reported in the ASTM data file. This is indicated by the data in Table 10. Since these compounds probably exist over a range of compositions around TiSi , variation in the line positions is not unexpected.

The samples shown in Figures 18 and 19 were oxidized at 1000°C in an atmosphere with an oxygen partial pressure of 0.2. The character of the growing oxide film was highly dependent on the composition and density of the sample. The sample which had a density of 96 percent of theoretical value showed three distinct oxide regions on the surface during the initial oxidation period.



Figure 18. Micrograph of Etched TiSi, 96 percent of Theoretical Density, 1600 X.



Figure 19. Micrograph of Etched TiSi, 91 percent of Theoretical Density, 1600 X.

Table 10

Comparison of Observed and ASTM X-ray

Data for TiSi

<u>Experimental</u>		<u>ASTM</u>		<u>Identification(hkl)</u>
<u>2θ</u>	<u>I/I₁</u>	<u>2θ</u>	<u>I/I₁</u>	
23.85	50	-	-	*
30.05	50	-	-	*
33.41	66	33.66	70	TiSi
37.15	100	37.29	100	TiSi
38.56	93	38.85	70	TiSi
39.15	100	39.30	100	TiSi ₂ (311)
41.29	113	41.54	80	TiSi
42.35	150	42.40	70	TiSi ₂ (004)
42.98	250	43.46	90	TiSi ₂ (022)
45.35	20	45.72	60	TiSi
46.20	80	46.53	80	TiSi
50.12	47	50.52	80	TiSi
59.51	13	59.94	70	TiSi
64.65	13	65.28	80	TiSi
69.95	13	70.24	70	TiSi

*These peaks found in all TiSi₂ samples.

In the area of a hole, a large clump of yellow crystalline material forms after 15 minutes at temperature. On the TiSi_2 phase, a transparent vitreous film is observed. The TiSi region is covered with a film which appears transparent but does not show the bright interference colors observed with TiSi_2 . Colors are observed; however, they are quite dull. X-ray analysis of the surface shows strong TiO_2 lines, TiSi and a small amount of TiSi_2 .

As the time of oxidation increases, the color of the transparent region changes corresponding to changes in thickness. The number and size of the yellow crystalline islands increase with reaction time. After 100 hours, the sample is covered with an opaque, adherent, pale yellow oxide. On microscopic examination, there are bright yellow crystalline islands amidst the paler yellow matrix. These areas appear to correspond to the holes observed in the unoxidized sample. The pale yellow matrix also appears to be crystalline. X-ray analysis shows strong TiO_2 and weak TiSi peaks.

When a sample of lower density, 90% of theory, is oxidized, the surface is covered with the yellow crystalline oxide after about five hours. In the initial stage of oxidation, approximately 0.1 hours, a transparent, purple film is formed. As the time increases, the yellow crystalline areas form and increase in size. At 1.0 hour, TiO_2 is strongly observed in the X-ray pattern.

The infrared spectrum of the growing oxide was obtained at 0.2, 0.5, 1.0, 2.25 and 4.0 hours of oxidation. Using 5X ordinate expansion, the characteristic peaks of amorphous SiO_2 are observed at each time. The peaks are shifted however, to lower frequencies. The absorption normally observed at 1250 cm^{-1} is shifted to 1180 cm^{-1} and that

normally found at 1100 cm^{-1} is found at 1050 cm^{-1} . No absorption is observed at 800 cm^{-1} . The lower frequency of the Si-O absorption indicates a less dense, or more impure, SiO_2 film. The lack of a Si-Si vibration at 800 cm^{-1} lends support to this conclusion. A broad absorption is also observed at 950 cm^{-1} . A small peak at 670 cm^{-1} , characteristic of TiO_2 , is also obtained. The position of all the peaks remains fairly constant as the oxidation time is varied up to four hours. Beyond this time, a spectrum cannot be obtained as the film is opaque and rough, apparently giving rise to diffuse reflection which is not picked up by the detector.

Several significant observations can be made from these data. The most important is that TiSi forms a protective oxide layer at a temperature of 1000°C and an oxygen partial pressure of 0.20. The crystallization and growth rate of the TiO_2 is strongly dependent on the number of holes in the sample surface. No crystalline forms of SiO_2 are observed in the X-ray diffraction patterns even after 100 hours of oxidation.

The initial amorphous SiO_2 part of the film is quite impure and of low density. Apparently the SiO_2 remains amorphous but is surrounded by so much crystalline TiO_2 that it cannot be observed in the infrared after four hours. The presence of the absorption at 950 cm^{-1} indicates considerable Ti-O-Si bonding in the amorphous region.

The observed weight gain for the TiSi wafers is also strongly dependent on surface quality. The data indicated in Figure 20, by the upper curve, is for the low density sample, while the lower curve is for the high density sample. When the square of the weight gain is plotted against oxidation time, a straight line can be drawn (see Appendix D).

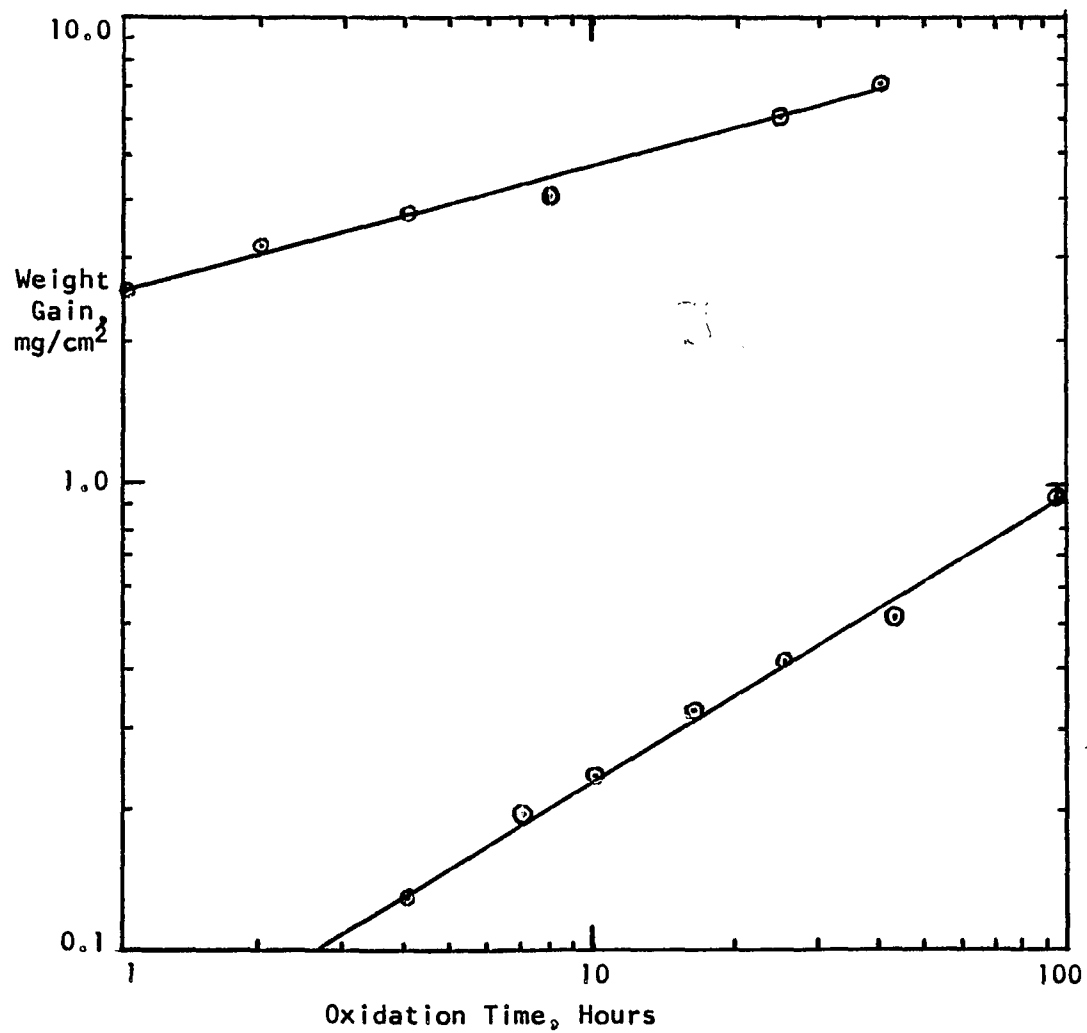


Figure 20. Oxidation Weight Gain Data for TiSi

The equations for the two runs are:

$$\text{Sample with many holes: } x^2 = 0.10t + 0.80$$

$$\text{Sample with few holes: } x^2 = 0.0088t - 0.0480$$

The presence of a greater number of holes in the surface causes an increase in the rate constant by a factor of 10.

2. Ti_5Si_3

Ti_5Si_3 is commercially available from CERAC Inc. The technique used in preparing the disilicide proved to be unsuccessful for the Ti_5Si_3 . With a sintering temperature as high as 1700°C for 15 minutes, wafers of low density (~ 75 percent of theory) are obtained. The addition of 0.5 percent titanium as a sintering aid does not result in any improvement of the density. When titanium is added, a layer of yellow TiO is formed on the bottom of the sample surface.

In order to get samples of reasonably high density, it was necessary to prepare Ti_5Si_3 directly from the elements. Titanium and silicon are reacted at 950-1100°C in a vacuum of 10^{-4} Torr. A vigorous exothermic reaction occurs. Heating is stopped when the temperature of the reactants reaches 950°C. Within a minute, the temperature climbs to 1100°C. The spongy product is ground, mixed with binder, compacted and sintered. Successful sintering of the pressed wafers is achieved at 1700°C. Sample density as determined by water displacement is 90 percent of theoretical. The polished surface appears mirror-like.

A typical micrograph of the surface is shown in Figure 21. There are more holes in these samples than in either the TiSi or TiSi_2 . In addition, there are considerable microcracks in the surface. Only one phase can be observed in the hole-free region. X-ray analysis indicates Ti_5Si_3 . Typical data are shown in Table 11. The peak positions vary



Figure 21. Micrograph of Etched Ti₅Si₃, 90 percent of Theoretical Density, 320 X.

Table 11

Comparison of Observed and ASTM X-ray
Data for Ti_5Si_3

<u>Experimental</u>		<u>ASTM</u>		<u>Identification (hkl)</u>
<u>2θ</u>	<u>I/I_1</u>	<u>2θ</u>	<u>I/I_1</u>	
27.71	6	27.68	7	$\text{Ti}_5\text{Si}_3(200)$
35.00	17	35.04	14	$\text{Ti}_5\text{Si}_3(002)$
37.12	39	37.24	47	$\text{Ti}_5\text{Si}_3(210)$
37.71	25	37.68	30	$\text{Ti}_5\text{Si}_3(102)$
41.06	100	41.02	100	$\text{Ti}_5\text{Si}_3(211)$
42.13	39	42.08	38	$\text{Ti}_5\text{Si}_3(300)$
42.80	93	42.76	98	$\text{Ti}_5\text{Si}_3(112)$
61.55	11	61.52	18	$\text{Ti}_5\text{Si}_3(222)$
66.81	18	66.76	29	$\text{Ti}_5\text{Si}_3(213)$
68.79	4	68.76	12	$\text{Ti}_5\text{Si}_3(402)$

slightly from the ASTM values while the intensities are almost identical. This is probably due to the fact that the Ti_5Si_3 grain size is quite small. For the larger grained TiSi_2 , the orientation of the sample with respect to the beam changes the reflected intensities.

Two wafers with the surface structure indicated in Figure 21 were oxidized at 1000°C in an oxygen-argon atmosphere with an oxygen partial pressure of 0.20. After about 0.5 hours at temperature, the sample is almost entirely covered with an opaque, yellow oxide. Microscopically, there are small areas where a transparent oxide film is present. X-ray analysis on the surface shows the Ti_5Si_3 substrate and the major TiO_2 (rutile) peak at $2\theta = 27.46^\circ$. This peak is due to constructive interference from the 110 plane.

The infrared spectrum at 0.5 hours is somewhat different from that obtained when TiSi_2 was oxidized. The usual SiO_2 absorption are observed at 1150, 1050 and 450 cm^{-1} . They are, however, extremely broad and of low intensity. The highest intensity absorption was observed at 885 cm^{-1} . This would appear to be the band due to the Ti-O-Si vibration observed at 940 cm^{-1} in the oxide on TiSi_2 . The shift to the lower frequency could be due to the presence of a greater concentration of titanium, either in or around the amorphous SiO_2 regions.

After about 20 hours at temperature, the surface is completely covered by an opaque, yellow oxide. X-ray analysis indicates only TiO_2 . In this case, the intensities of the low angles from $2\theta = 27^\circ$ to 35° are considerably lower than the standard values. The Ti_5Si_3 substrate lines are not observed. The peak positions of the TiO_2 in the X-ray also appear to be decreasing, indicating an increase in lattice spacing. Some typical data are shown below:

Oxidation Time, Hrs	2 θ			
ASTM Standard	27.45	36.05	41.22	54.33
0.7	27.40	36.03	-	54.25
24.5	27.40	36.05	41.20	54.23
44.5	27.35	36.00	41.15	54.]]
100.5	27.27	35.83	41.02	54.10

In addition to this shift to lower values of 2θ , the peaks are also very much broader. An infrared spectrum of the surface could not be obtained since it appears that diffuse reflection from the surface is occurring.

The oxide formed on Ti_5Si_3 is thick enough to be seen in cross section under a light microscope. Using polarized light, the result shown in Figure 22 was obtained. Several distinct layers are observed, with additional phases within each layer. In order to determine the composition of the different structures, considerable additional effort involving additional equipment would be required.

The weight gain data for the oxidation of Ti_5Si_3 at 1000°C and 0.2 atmospheres oxygen pressure is shown in Figure 23. Two samples were oxidized, one with a density of 82 percent of theory, the other 88 percent. Examination of the surfaces indicated about the same hole density. The weight gains observed agreed within 5 percent.

The value of the exponent in the equation $X^n = kt$ after approximately 0.5 hours of oxidation is 5.7. In the initial period, up to 0.5 hours, the slope is considerably greater with a value as high as 2 being obtained between 0.1 and 0.2 hours.

When the square of the weight gain is plotted against oxidation

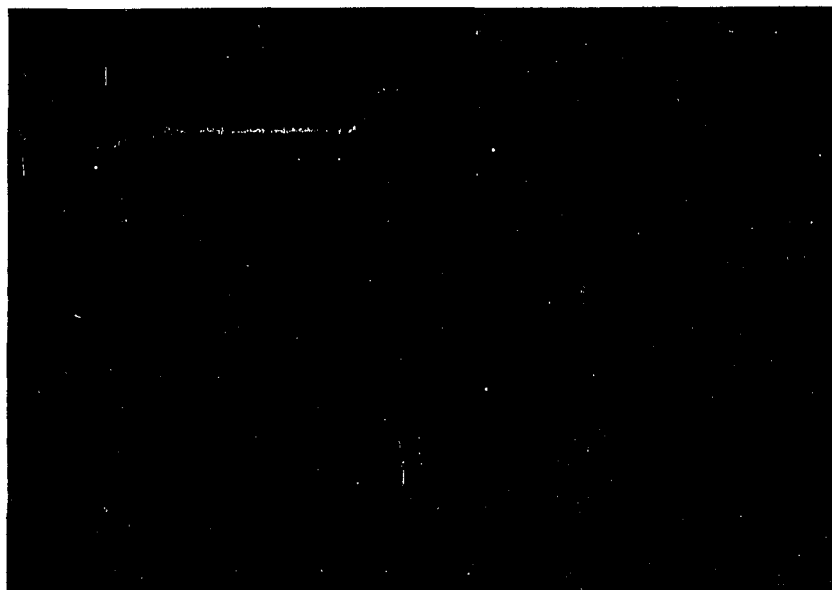


Figure 22. Cross-section of Oxide Formed on Ti_5Si_3 Oxidized at 1000°C for 45 Hours, 1600 X.

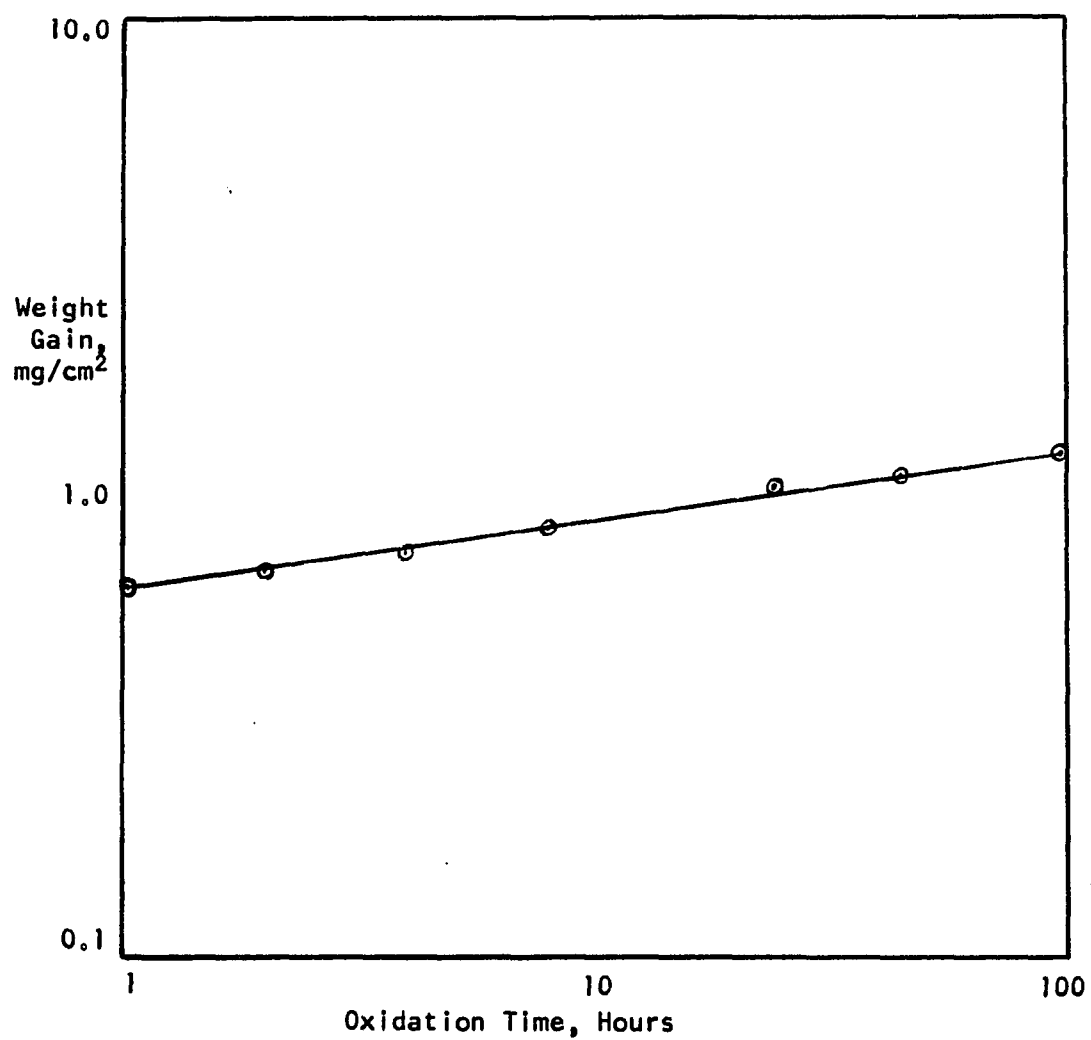


Figure 23. Oxidation Weight Gain Data for Ti_5Si_3

time, a straight line with the equation

$$x^2 = 0.65t + 84$$

can be obtained (see Appendix D).

The important factor in the oxidation of Ti_5Si_3 is that it forms a protective oxide layer at 1000°C for oxidation times up to 120 hours.

3. $TaSi_2$

An attempt was made to prepare wafers from $TaSi_2$ powder obtained from CERAC Inc. The density of the sintered samples was only 70 percent of the theoretical value. $TaSi_2$ was then prepared directly from tantalum and silicon powders at 1000°C in a vacuum of 10^{-4} Torr. Wafers made from this material had densities of 90 percent of the theoretical value. X-ray analysis indicates $TaSi_2$ with a trace of Ta_5Si_3 .

Two samples were oxidized at 1000°C in an oxygen-argon atmosphere with an oxygen partial pressure of 0.2. After 1 hour at temperature, a yellow oxide is formed around the sample edges. The faces of the sample are covered by a blue, transparent film. After 5 hours, the oxide begins to spall from the edges, while the faces begin to show yellow oxide. After 10 hours, heavy spalling occurs on both the edges and faces. X-ray analysis of the surface indicates $\beta-Ta_2O_5$ and a trace of the $TaSi_2$ substrate. No weight gain data was obtained. It is not clear whether $TaSi_2$ is non-protective or whether the small amount of Ta_5Si_3 present in the sample causes the deterioration.

4. $TaSi_2$ - $TiSi_2$

Several wafers of a mixture 60 mole percent $TaSi_2$ and 40 mole percent $TiSi_2$ were prepared from homemade $TaSi_2$ and $TiSi_2$. Sintering at 1400°C yields a sample with a density of approximately 90 percent of

the theoretical value. X-ray analysis of the polished surface indicates only TaSi_2 and TiSi_2 . The TaSi_2 lines are identical to the ASTM values while the TiSi_2 lines are found at lower values of 2θ . This is consistent with the results obtained on the pure samples.

Two samples were oxidized at 1000°C and 1300°C in an oxygen-argon atmosphere with an oxygen partial pressure of 0.20. At 1000°C and 45 hours of oxidation, a protective oxide layer is formed. A micrograph of the oxide is shown in Figure 24. The large light regions exhibit the interference colors typical of amorphous SiO_2 . Under polarized light, the large dark regions appear bright yellow, typical of TiO_2 . The smaller dark regions appear brown in polarized light. X-ray analysis indicates the original substrate and TiO_2 (rutile). There is no evidence of crystalline Ta_2O_5 or SiO_2 . The weight gain observed after 45 hours is approximately 1 mg/cm^2 .

At 1300°C and 45 hours, a protective oxide layer is also formed. In this case, no regions of transparent oxide are present. X-ray analysis indicates the substrate, TiO_2 (rutile) and SiO_2 (α -cristobalite). No Ta_2O_5 is observed. The weight gain after 45 hours is approximately 1.5 mg/cm^2 .

D. TiO_2 - SiO_2 Solubility and Glass Formation

In order to be able to better characterize the oxide growing on TiSi_2 , a study was made of the reactions occurring in the TiO_2 - SiO_2 system at elevated temperatures. A detailed description of the results is given in Appendix E. The results pertinent to the oxidation study will be described here.

The phase diagram for the TiO_2 - SiO_2 binary system was shown earlier in Figure 1. These data indicate a maximum solubility of TiO_2 in SiO_2



Figure 24. Micrograph of Oxide Formed on
0.6 TaSi₂-0.4 TiSi₂ Oxidized at
1000°C, 320 X.

of 10 wt. percent at the eutectic temperature of 1540°C. These studies were carried out in air.

In order to confirm these results and obtain samples for analysis, a number of wafers containing 10 wt. percent TiO_2 were heated at 1550°C for 15 minutes at 10^{-4} Torr. The sample coalesces but does not bond to the alumina support dish. X-ray analysis of the glassy-blue surface indicates the material is amorphous. The infrared spectrum is the same as the SiO_2 charged with one major exception. A broad absorption is observed at 935 cm^{-1} . If a solid solution or glass is formed, a Ti-O-Si vibration would be expected. Zeitler and Brown (44) have reported results on the infrared spectra of organic-titanium-silicon compounds. They attribute an absorption at $919\text{--}925\text{ cm}^{-1}$ to a Ti-O-Si vibration. They also show the Si-O stretching vibration at 1110 cm^{-1} , or nearly the same as in amorphous SiO_2 . While this is not construed as positive proof, it appears likely that the absorption observed at 935 cm^{-1} in this study is due to a Ti-O-Si vibration. Since titanium is classified as a network modifier (11), it is likely that a substitutional solid solution or glass is formed.

When the concentration of TiO_2 is increased to 20 wt. percent and heated at 1550°C, TiO_2 is observed in the X-ray analysis. This confirms the solubility level of 10 wt. percent TiO_2 reported by Ricker and Hummel (21).

An interesting and unexplained result is obtained when a sample containing 10 wt. percent TiO_2 is heated in vacuum at 1200°C. While the TiO_2 lines disappear from the X-ray pattern, the infrared spectrum shows only the pure SiO_2 . No absorption is observed at 935 cm^{-1} . Apparently, some type of physical segregation is occurring and not

solution. When this sample is reheated in air at 1200°C, the color turns from blue to the original white and the TiO_2 lines reappear in the X-ray pattern.

VIII. Discussion

A. Introduction

The purpose of this study was to (1) obtain data on the oxidation of bulk TiSi_2 in the temperature region 300-1300°C, (2) develop a mechanism to describe the oxidation and (3) relate this mechanism to results obtained with other silicides and determine whether a consistent theory of oxidation protection can be applied to this general class of materials.

Suitable samples for oxidation studies were made using the techniques of powder metallurgy. The silicides are prepared by direct reaction of the elements in vacuum at approximately 1000°C. The use of polymethylmethacrylate binder allows pressing of the powdered silicide into one inch diameter wafers at 5-10 tsi. Sintering at 1400°C in vacuum yields samples with densities of 95 percent of the theoretical value. Polishing with diamond paste results in mirror-like surfaces. Small holes and a trace amount of a second phase are usually observed upon metallographic examination. This cold pressing technique is superior to the hot pressing method previously used in preparing other silicide pellets (45) in that no carbon contamination of the sample occurs.

In an oxidation reaction, there are four steps which are involved before reaction can occur. Initially, there is transport of the oxygen from the gas phase to the solid surface followed by adsorption onto the surface. One or more species then diffuse through the oxide layer with subsequent reaction at an interface. Either of these steps may be rate controlling.

In this study, gas phase transport can be neglected since no difference in rate is observed between samples oxidized in stagnant and rapidly flowing gases. In addition, phase boundary reaction control is not likely since these phenomena normally give rise to reaction rates which are independent of film thickness. These data indicate, especially at low temperatures, that the reaction rate is highly dependent on film thickness. Some form of transport of one or both of the reacting species through the oxide film appears to be the rate controlling step. These conclusions are valid only for oxidation times which are greater than those for which a different initial mechanism may prevail. The rate at which diffusion through the oxide occurs depends on the structure of the oxide film.

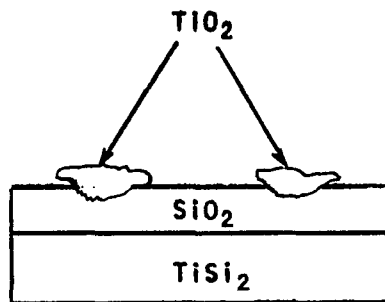
B. High Temperature Model for TiSi_2 Oxidation

Between 1000 and 1300°C, the oxide structure consists of crystalline TiO_2 islands growing out of a slightly impure silica matrix. The rate data for samples with few holes indicate parabolic behavior with an activation energy of 21.3 kcal. The weight gain observed for TiSi_2 at any time of oxidation is approximately 50-70 percent greater than that obtained when silicon is oxidized. The question to be answered is how does diffusion occur through the oxide growing on TiSi_2 .

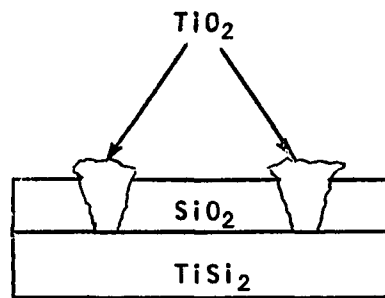
Two cases can be considered. These are illustrated in Figures 25a and 25b. In Figure 25a, the entire silicide surface is covered by vitreous SiO_2 with the TiO_2 islands on top of the SiO_2 film only. In order for reaction to occur, it is necessary for diffusion to occur through the amorphous silica region. When compared to silicon oxidized for the same time, the thickness of the SiO_2 film on both the silicon

Figure 25

Possible Oxide Film Structures



(a)



(b)

and titanium disilicide would be the same since diffusion through the film is rate controlling. The weight gain for the silicide, however, would be 50 percent greater since for each silicon atom oxidized, 0.5 atoms of titanium are oxidized. The TiO_2 island growth would occur by diffusion of titanium through the silica to the TiO_2 islands. The weight gain, assuming this mode of transport, is what is experimentally observed.

The growth mechanism for the film shown in Figure 25b would be by parallel diffusion through both the amorphous silica and crystalline TiO_2 regions. In this case, the TiO_2 islands extend through to the TiO_2 substrate. Kofstad (46) shows the parabolic constant for titanium oxidation at 1000°C as $0.6 (\text{mg}/\text{cm}^2)^2/\text{min}$ ($3.6[\text{mg}/\text{cm}^2]^2/\text{hr}$). At this temperature, it appears that either the titanium or oxygen may be the diffusing species for titanium oxidation. The parabolic rate constant for silicon oxidation as reported by Deal and Grove (29) has been given as $1.57 \times 10^{-4} (\text{mg}/\text{cm}^2)^2/\text{hr}$. If the TiO_2 covers 10 percent of the sample surface, the contribution to the overall rate through the TiO_2 would be greater than that through the SiO_2 by a factor of about 10^4 . If there were pores or channels between the crystalline TiO_2 and the amorphous SiO_2 , this ratio would be greater still. For the case described in Figure 25b then, the weight gain would be 100 times greater than that actually observed.

This calculation indicates that diffusion occurs through an amorphous silica film in which TiO_2 islands grow on the oxide-gas surface, as illustrated in Figure 25a. This is further confirmed by the fact that the activation energy for the reaction, 21.3 kcal, is very near the 28.5 reported for silicon oxidation (29).

Light microscope examination of a sample cross-section indicates TiO_2 growing on top of the film in the manner of Figure 25a and in some areas, particularly at holes, through the film, as in Figure 25b. The resolving power of the light microscope, however, is not sufficient to determine whether these islands do indeed go through the film to the substrate or whether they are separated from the substrate by a thin silica layer.

At 1000-1300°C, the number of holes in the sample greatly affects the oxidation rate. Observable crystallization of the TiO_2 occurs at an earlier time of oxidation when the number of holes is increased. When the square of the extended time weight data for samples with many holes is plotted against time, a straight line is obtained in most cases. The line does not pass through the origin. Apparently a two stage mechanism is involved: An initial rapid oxidation occurring before significant crystallization, followed by a slower parabolic reaction. If indeed the TiO_2 crystalline islands are nearly separated from the base by the amorphous SiO_2 , the initial rapid reaction could be due to TiO_2 channels through the film. Once significant growth has occurred, the crystalline TiO_2 would be forced up and onto the growing amorphous silica matrix. Diffusion would then be through a primarily silica film.

C. Low Temperature Model for TiSi_2 Oxidation

Measurable oxidation of TiSi_2 begins at approximately 300°C. The thin oxide film appears to be SiO_2 with isolated areas where impurities have oxidized. Since the weight gains are quite low and a competing reaction takes place, a quantitative interpretation is not justified.

At 600°C, an impure, amorphous SiO_2 film, exhibiting interference

colors which vary with TiSi_2 grain orientation, is formed. Infrared analysis indicates the presence of Ti-O-Si bonding in the oxide film.

The kinetic data at 600°C are characterized by a rapid initial rate followed by extremely small reaction rates. No effect is observed as the number of holes in the surface is varied or as the partial pressure of oxygen is changed from 0.2 to 1.0.

Since the oxide thickness varies with surface orientation, the surface reaction between the silicide and oxygen is probably rate controlling for some initial period. Since the thickness at extended times does not change appreciably, this initial oxide makes a significant contribution to the optical interference.

These results appear to indicate that after the initial surface reaction control, some form of diffusion through the growing oxide film is the rate controlling step. For oxidation times of up to 300 hours, the plot of the square of the weight gain versus time for the 600°C data shows no straight line regions. This indicates that normal bulk diffusion is not rate controlling.

It is proposed that the mechanism of growth at 600°C after the initial rapid rate is one of diffusion control with a variable diffusivity. Initially, the oxide growth occurs by bulk and short circuit diffusion. As the oxidation time increases, the short circuit paths become blocked and bulk diffusion controls. If this were the mechanism, the plot of X^2 versus t would give a straight line at extended times. If it is assumed that the slope of the data obtained after 200 hours of oxidation is constant, a parabolic rate constant of $85 \times 10^{-7} \text{ (mg/cm}^2\text{)}^2\text{/hr}$ is obtained.

Since the high temperature data are essentially for diffusion through a silica film, extrapolation using the Arrhenius plot should give an estimate of the parabolic rate constant at 600°C. These data, along with data for silicon oxidation, are shown in Table 12. The experimental value of $85 \times 10^{-7} \text{ (mg/cm}^2\text{)}^2\text{/hr}$ is extremely close to the $40 \times 10^{-7} \text{ (mg/cm}^2\text{)}^2\text{/hr}$ obtained by extrapolating the high temperature data. Since the low temperature silica is impure, i.e., contains TiO_2 , diffusion would be easier giving a larger parabolic rate constant.

The values obtained for TiSi_2 cannot be compared directly with the results observed for silicon since the latter shows negligible oxidation at 600°C. However, extrapolating the data of Deal and Grove (29) to 600°C gives a value of $4.3 \times 10^{-5} \text{ }\mu^2\text{/hr}$ or assuming an oxide density of 2.2 gms/cm^3 , $5. \times 10^{-7} \text{ (mg/cm}^2\text{)}^2\text{/hr}$ for the parabolic rate constant. This value is considerably smaller than that obtained experimentally or by extrapolation for TiSi_2 . This could indicate that either the diffusivity through the low temperature oxide is greater due to the presence of titanium or that the slopes from the X^2 versus t plots are not constant. In either case, the consistency of the numerical values adds evidence to the proposed variable diffusivity model. Certainly the validity of the extrapolation for both the disilicide and silicon data is questionable.

A similar treatment was carried out on the data obtained at 800°C. These data are also shown in Table 12. These results are in line with those described for the 600°C data.

Nothing definitive can be said concerning the mechanism by which the diffusivity decreases. This could be due to the closing of pores

Table 12

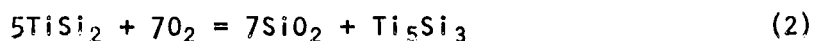
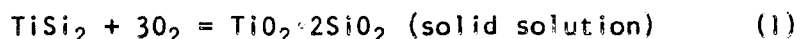
Comparison of Parabolic Rate Constants
for TiSi_2 and Silicon Oxidation

Temp °C	$k_p \text{ (mg/cm}^2\text{)}^2\text{/hr}$		
	TiSi_2		Silicon*
	Experimental	Extrapolated	
1300	17.4×10^{-4}	-	-
1200	8.72×10^{-4}	-	6.04×10^{-4}
1000	3.52×10^{-4}	-	1.57×10^{-4}
800	0.26×10^{-4}	0.7×10^{-4}	0.147×10^{-4}
600	85×10^{-7}	40×10^{-7}	5×10^{-7}

*Data from Deal and Grove (29). Calculated from $\mu^2\text{/hr}$ assuming oxide density of 2.2 gms/cm^3 .

by reaction in the pores or by compressive stresses in the oxide. It could also be due to ageing of the oxide where interstitial spaces created at the time of oxidation are gradually closed. In either case, the presence of the short circuit paths is due to the low atomic mobility in the oxide at low temperature. While there is no evidence indicating the presence of pores in the oxide, the study of Ing_o et al. (21) on the structure of the oxide film on silicon indicates microchannels. This type of defect would be more likely to occur in the impure silica films considered here.

One of the most interesting and unique results in this study is the formation of an entirely amorphous film at 600°C. Since crystalline TiO₂ is not observed, the titanium is either trapped in the silica matrix or has formed a lower silicide layer beneath the growing oxide film or a combination of both. The possible reactions that could occur are:



Little can be said about a preferred reaction from the thermodynamic data available. The free energy change of reactions (1) - (3) are almost identical (see Appendix F). No thermodynamic data is available on silicon dissolution in titanium disilicide.

The infrared analysis indicates that reaction (1) to form a TiO₂·2SiO₂ solid solution is likely. The crystallization of TiO₂ observed when a sample oxidized at 600°C is heated to 1200°C in a reduced oxygen pressure atmosphere contributes to the validity of titanium

trapped in the silica. The formation of a $\text{TiO}_2\text{-SiO}_2$ solution requires that 40 wt. percent TiO_2 (33 atomic percent) be dissolved if a stoichiometric reaction occurs. While the phase diagram for the system shows a maximum solubility of 10 wt. percent TiO_2 in SiO_2 at 1500°C , it is conceivable that in a solid-state reaction of this kind, 40 wt. percent TiO_2 could be retained in a metastable solution. The lack of crystallization indicates that the energy required for either nucleation or diffusion of the titanium is too great. If reaction (1) is correct, then the implication is that the energy required for oxygen diffusion and surface reaction is less than for titanium diffusion.

A combination of reactions (1) and (4) would result in a solution in which the TiO_2 concentration would be less than 40 percent. Reaction of dissolved silicon at the surface would also result in diffusion of dissolved silicon from the interior of the silicide. Whether this rate would be significant or whether there is sufficient dissolved silicon in the samples is not known. It is also not clear whether dissolved atomic silicon would be more active than bulk silicon which undergoes negligible oxidation at 600°C .

Were reactions (2) or (3) to occur, the oxide formed would be pure SiO_2 . A combination of (1) and (2) or (3) would result in an oxide film with titanium dissolved in the film and a lower silicide layer beneath the oxide. The thickness of this lower silicide, assuming reaction (2) with some typical weight gain data is approximately 0.4 micron. Calculations (Appendix B) show that this thickness Ti_5Si_3 would diffract only 1 percent of the incident X-radiation. Almost all the diffracted energy is attributable to the TiSi_2 substrate. This would also be

applicable to changes in the TiSi_2 lattice parameters as silicon is removed assuming reaction (4) is valid. The thickness of the silicon-free region would also probably be too small to be observed.

These considerations indicate that either reaction (1) or a combination of (1) with (2), (3) or (4) is occurring at 600°C .

D. TiSi and Ti_5Si_3 Studies

Wafers of TiSi and Ti_5Si_3 were prepared using the techniques of powder metallurgy. Purchased Ti_5Si_3 cannot be sintered to a sufficiently high density. Preparing the TiSi and Ti_5Si_3 directly from the elements by reaction in vacuum provides suitable material. TiSi contains small amounts of TiSi_2 while the Ti_5Si_3 surface has many holes and microcracks. On oxidation, these lower silicides form protective, opaque yellow oxide films. X-ray analysis indicates crystalline TiO_2 (rutile). A plot of the weight gain data as X^2 versus t , gives a straight line which does not extrapolate through the origin.

Since few runs were made, no model can be proposed for the oxidation although comparison can be made with titanium, TiSi_2 and silicon.

The parabolic rate constants for the straight line region of the weight gain data are shown in Table 13 along with those for silicon, TiSi_2 and titanium. The general trend is clear. The value for TiSi_2 is close to silicon. The value for TiSi is 30 times greater than for TiSi_2 , although still quite small, while Ti_5Si_3 is approaching that for titanium. If the model proposed for TiSi_2 is correct, then as the amount of titanium in the substrate is increased, it might be expected

Table 13

Parabolic Rate Constants at 1000°C for Materials
in the Titanium-Silicon System

<u>Material Oxidized</u>	<u>$k_p, (\text{mg}/\text{cm}^2)^2/\text{hr}$</u>
Silicon	$1.57 \times 10^{-4}{}^a$
TiSi ₂	3.52×10^{-4}
TiSi	90×10^{-4}
Ti ₅ Si ₃	0.65
Titanium	$3.6{}^b$

^aData of Deal and Grove (29)

^bSee Kofstad (59)

that some of the islands would extend through the oxide to the substrate. This would result in a large increase in the parabolic rate constant. While TiSi is covered with an opaque yellow oxide, the low value for the rate constant indicates that there may be an amorphous SiO₂ layer below the TiO₂ covering most of the surface. Microscopic examination of the oxide on Ti₅Si₃ in cross-section does indicate a layered structure. The composition of this structure was not determined.

E. Mechanism for Protective Film Formation

The results of this study have indicated a mechanism which describes the growth rate of the oxide film formed on TiSi₂ during its oxidation. Of additional importance is what is the characteristic or characteristics that account for the ability of this system to form a protective, adherent oxide.

The oxidation behavior of the titanium silicides is in marked contrast to MoSi₂ which has been studied extensively and also to most of the other silicides which have been given cursory examinations. In polycrystalline MoSi₂, the presence of MoO₃ in the oxide at temperatures of 300-600°C results in rapid deterioration of the sample. Berkowitz-Mattuck, et.al. (18) attribute this "pest" phenomena to the pressure exerted by the growing oxide in cracks on the sample surface. Both MoO₃ and SiO₂ are formed. Above 600°C, the MoO₃ volatilizes and a protective silica film which bridges the cracks is formed. Berkowitz-Mattuck, et.al. suggest that the failure of some silicides, including MoSi₂, to form a protective film is due to microcracks in the substrate and the presence of a duplex film of both oxides.

For the case of TiSi_2 , a protective film is formed even though both oxides are present. The presence of imperfections in the surface, particularly Ti_5Si_3 which has considerable holes and microcracks, results in an increase in the oxidation rate. However, an adherent oxide film is still formed. The present study suggests that while the presence of cracks in the sample presents high energy nucleation sites which increases the reaction rate, the compatibility of the oxides is the more fundamental requirement for the formation of a protective oxide. The fact that TiO_2 is partially soluble in SiO_2 appears to be quite significant.

Two of the more important factors which determine whether a glass or solid solution can be formed are ionic size and charge. Titanium, a network modifier, has the same charge as silicon. The ionic size of titanium is greater than silicon and usually requires sixfold coordination. The solid solution studies on the TiO_2 - SiO_2 system have indicated, however, that titanium can have fourfold coordination and replace silicon in the SiO_2 network. At low oxidation temperatures, this results in the formation of a titania-silica glass. At high temperatures, this allows titanium to diffuse through the silica film to the nucleation sites without disrupting the silica network. This probably occurs by a vacancy diffusion mechanism since the interstices are considerably smaller than could conveniently accommodate the titanium atom.

The infrared studies of the amorphous silica at temperatures over 800°C indicate that there is some titanium in the silica. The mobility of titania at temperatures over 1000°C is evidenced by the

ease at which it sinters when fired in bulk form.

In addition to the solubility effect, the ability of the crystalline TiO_2 to exist and grow upward and out of the SiO_2 without cracking the film is critical.

The lack of compatibility of the oxides formed in the oxidation of MoSi_2 in the 300-600°C temperature region can be due to many factors. The inability of the molybdenum ion to form a glass or solid solution might be significant. The ionic radius of Mo^{5+} is 0.62 Å compared to 0.68 Å for Ti^{4+} (11). The ionic field strength of the molybdenum ion classifies its function in glasses as an intermediate ion, i.e., it cannot usually form a glass but can take part in the network. Since titanium with a slightly larger ionic radius can replace silicon in the silica network, the size does not appear to hinder glass formation. The ionic charge of +5, however, would result in a structure which would not be neutral and hence unstable. This charge factor might also prevent tantalum and columbium from forming glasses. The silicides of these materials also form non-protective oxide films when oxidized.

In the preparation of silicide coatings on tantalum or columbium, it would seem desirable to add modifiers with a +3 charge in order to form an oxide with the capability of a neutral structure. The balancing of the charge, obviously, does not guarantee glass formation but would be desirable in the event the glass-forming ability were there.

The concept of oxide compatibility is quite complex. The structural considerations which result in the formation of a

glass are still being debated. In the oxidation of the silicides, the compatibility involves both glass formation and coexistence of a glass with a crystalline oxide. An extensive study of the factors involved in the compatibility of binary oxides is beyond the scope of the present work.

IX. Conclusions

In the temperature range 300-1300°C at oxygen pressures of 0.2 to 1.0 atmosphere, TiSi_2 forms a protective silica based oxide layer.

The oxidation rate and to a smaller extent the oxide structure are highly dependent on the density and quality of the sample surface at temperatures over 1000°C.

In the temperature range 600-800°C, the oxidation rates fall rapidly to very low values. At 1000-1300°C, the rate is parabolic with an activation energy of 21.3 kcal.

The lower silicides, TiSi and Ti_5Si_3 , also form protective oxides at 1000°C and 0.2 oxygen pressure. In this case, rutile is the major component in the film.

The underlying structural consideration which accounts for the formation of a protective oxide film on titanium silicides appears to be the limited solubility and compatibility of the oxides in the TiO_2 - SiO_2 system.

X. APPENDIX

A. Infrared Spectroscopy

I. Introduction

A substance is active in the infrared region of the spectrum if atomic vibrations giving rise to a change in the dipole moment are present. If the frequency of the radiation corresponds exactly to the frequency of the atomic motion, all or part of the radiation will be absorbed by resonance. The molecule may have either a permanent or a temporary dipole moment. In general, covalent bonding between unlike atoms gives rise to infrared absorption while ionic bonding does not.

In the study of the structure of solids, there are two types of vibrations that give rise to absorption in the infrared region. These are vibrations characteristic of the individual molecules and those characteristic of the symmetry of the unit cell. The latter are known as lattice vibrations and are only found in solids.

In solids, the molecular type vibrations are of two kinds. These are stretching and bending vibrations. The stretching vibration is the back and forth motion of two or three atoms along a valence bond. The second type, the bending vibration, is due to motion across the valence bond between atoms.

In elucidating structure, there are three characteristics of the absorption peak that are considered. These are the intensity, position and half-width of the band.

There are a number of experimental techniques which can be used to study the infrared spectrum of solids. The two more common methods are absorption and reflection spectroscopy. Reflection spectroscopy is used extensively in glass studies because of the high absorptivity

of silica. When transmission studies are carried out, fine particles or very thin sheets are used. With powders, nujol mulls or KBr pellets are used.

In absorption or transmission spectroscopy, the position of the absorption peak is a direct measure of the resonant frequency. The position of a reflection peak, on the other hand, does not coincide with the absorption frequency. In order to obtain the resonant frequency, corrections involving the refractive index and extinction coefficient are required.

2. Infrared Spectra of Silicon Dioxides

The four major polymorphs of silicon dioxide that are of interest in this study are quartz, tridymite, cristobalite and vitreous silica. While the infrared spectra of these materials has been studied in bulk form for many years, its complete interpretation is not yet in hand. In this oxidation study, the two major objectives are to determine what form the silica is in and what is its purity.

One of the major problems encountered in the bulk infrared studies is the fact that SiO_2 is nearly opaque in the infrared region. For this reason, powders, either in KBr or nujol, are frequently used. In addition, reflection techniques are used quite often. It is difficult to compare data obtained by the different methods since particle size affects the peak structure and the reflection maxima do not correspond to absorption maxima.

Simon (47) has recently summarized the infrared studies on amorphous SiO_2 . The main absorptions are located at 1100, 800 and 465 cm^{-1} . The most intense band, that at 1100 cm^{-1} , has been

attributed to Si-O bond stretching. It has also been suggested (48) that the 800 and 465 cm^{-1} absorptions are due to Si-Si bond stretching and Si-O-Si bond bending, respectively. These two assignments are still open to question.

In addition to the three major peaks, very weak absorptions are observed at 1190 and 950 cm^{-1} . The significance of these absorptions is not well understood.

The absorption frequencies for amorphous silica are very similar to those obtained for the crystalline polymorphs. In the case of the crystalline modifications, the absorptions are usually sharper. α -quartz can be distinguished from amorphous silica by the presence of a doublet at 800 and 770 cm^{-1} (48). In a reflection study (49), the major Si-O vibration was found at 1065 cm^{-1} compared to 1100 cm^{-1} for amorphous SiO_2 . This same absorption was found at 1085 cm^{-1} in α -cristobalite. This material also shows an absorption at 1190 cm^{-1} (49). The infrared spectra of trydimite is very similar to that of amorphous silica (48). Both have the same number of absorptions.

The variation in the position of the 1100 cm^{-1} vibration among the polymorphic forms is also observed with the 460 cm^{-1} vibration (50). Vitreous silica shows a broad reflection at 465 cm^{-1} , α -quartz a sharp band at 455 cm^{-1} and α -cristobalite a band of intermediate halfwidth at 493 cm^{-1} .

3. Variation of Peak Position with Impurities in Silica

The effect of additions of Li_2O , Na_2O and K_2O on the position of the Si-O stretching vibration at 1100 cm^{-1} has been studied by Simon and McMahon (51). These materials cause rupture of some of the tetra-

hedral Si-O linkages resulting in "non-bridging" oxygen groups.

When 23 mole percent Li_2O is added to SiO_2 and a glass formed, the 1100 cm^{-1} absorption is considerably broadened. A new band also appears at 950 cm^{-1} . The addition of 22 mole percent K_2O causes a similar effect with the new peak at 1050 cm^{-1} . When the concentration of Na_2O is increased from 0 to 23 mole percent, the peak intensity decreases, the half-width increases and the absorption shifts to lower frequencies. This is characteristic of a disordering of the original SiO_2 structure. Above 23 mole percent Na_2O , a second peak emerges at 950 cm^{-1} . Beyond 33 mole percent Na_2O , two distinct bands at 940 and 1075 cm^{-1} are found. The peak at 1075 cm^{-1} may be attributed to Si-O⁻ or ⁻O-Si-O⁻ bond stretching vibrations.

4. Infrared Spectra of Titanium Oxides

The infrared spectra of rutile, anatase and Ti_2O_3 have been obtained by McDevitt and Baun (55). The study was made by preparing specimens of the oxides in nujol mulls. Anatase shows absorption peaks at 700 vb, 525 vb and 374; rutile at 695 b, 608 b, 423 and 352; while Ti_2O_3 has a single band at 650 cm^{-1} . As the authors point out, and as discussed earlier, the sharpness and exact position of the peaks is in part determined by the particle size used in the mulls.

5. Spectrophotometer Control Settings

There are four control variables which are to be optimized to yield absorption peaks whose positions are readable and reproducible. These are slit program, attenuator speed, scale expansion and scan time. These were varied as indicated in Table 14. The gain was held constant at 5, suppression at 7, source current at 0.66 and scale

Table 14

Variation of Spectrophotometer Control Setting

<u>Slit Program</u>	<u>Attenuator Speed</u>	<u>Scan Time</u>	<u>Peak Positions, cm^{-1}</u>		
2000	600	32	1255	1070	785
2000	525	32	1253	1068	780
1600	600	32	1252	1068	770
1200	500	32	1255	1062	775
1000*	1100	16	1152	1060	780
1600	550	32	1252	1068	780
2000	600	32	1255	1070	780
			<u>1253</u>	<u>1066</u>	<u>781</u>

*at 1X, all others at 5X

expansion at 5X. The peaks at 1065 cm^{-1} and 1253 cm^{-1} were, in each case, sharp and well formed. As indicated by these results, the location of the peak is quite reproducible even with the wide range of the control settings used. Based on these results, the settings used in this study are given in Table 15.

6. Detailed Data on the Oxide Formed on TiSi_2

Detailed infrared data on the oxide formed on TiSi_2 when oxidized at 600, 800, 1000 and 1200°C are given in Tables 16, 17, 18 and 19, respectively.

B. X-ray Diffraction

1. ASTM Data

The interplanar spacings and intensity ratios for the crystalline materials of interest in this study are reported in the ASTM Powder Diffraction File (52). These data are summarized in Tables 20-26. The diffraction angles (2θ) were obtained from the interplanar spacings using the tables in reference (38) with $\lambda = 1.54050\text{ \AA}$. The region of $2\theta = 20$ to 72° was scanned. Only these data are reported.

2. Sensitivity of the X-ray Method

X-ray diffraction was used to study the surface of the silicide wafers and also the glasses and solid solutions formed in the $\text{SiO}_2\text{-TiO}_2$ system. The major impurities in the silicides are either silicon, titanium or other silicides in the titanium-silicon system. Since compositional changes occur during sintering, a precise value for the sensitivity of the X-ray method to impurities was not determined. It appears that in the $\text{TiSi}_2\text{-Si}$ system, silicon concentrations as low as 0.5 weight percent can be determined.

Table 15

Infrared Control Settings

Scale expansion	1X	5X
Slit program	1000	2000
Attenuator speed	1100	600
Scan time	16	32
Gain	4.5	4.5
Suppression	7	7
Source current	0.66	0.66

Table 16

Infrared Results on Oxide Formed
on TiSi_2 Oxidized at 600°C

Sample	Pressure O_2	Oxidation Time, Hrs	Wt Gain, mg/cm^2	Absorption Maxima, cm^{-1}					
2a	0.2	61.5	0.134	1020	940	800	650	440	1150- 1200
2b(1)	0.2	125	0.395	1050	x	x	x	x	1220
2b(1)	0.2	125	0.395	1050	930	x	x	x	1220
6	1.0	54	0.0778	1040	920	800	660	-	1150- 1200
6	1.0	187	0.0898	1040	940	800	650	-	~1200
11	1.0	307	0.126	1010	920	800	-	435	1150

x: Region not investigated

Table 17

Infrared Results on Oxide Formed
on TiSi_2 Oxidized at 800°C

<u>Sample</u>	<u>Wt Gain, mg/cm²</u>	<u>Absorption Maxima, cm⁻¹</u>			
4a	0.07	1255	1060	-	-
4b	0.0676	1258	1060	-	-
9	0.139	1200	1020	780	430
10	0.0678	1255	1040	-	-

Table 18

Infrared Results on Oxide Formed
on TiSi_2 Oxidized at 1000°C

<u>Sample</u>	<u>Wt Gain, mg/cm²</u>	<u>Time of Oxidation, Hours</u>	<u>Peak Position, cm⁻¹</u>		
1a	0.186	97	1251	1058	788(?)
1b	0.221	97	1255	1065	780
1c	0.259	97	1258	1060	780
1d	0.152	49	1255	1070	780
1e	0.182	49	1255	1065	780
			1254±3	1065±4	780±0

Table 19

Infrared Results on Oxide Formed
on TiSi_2 Oxidized at 1200°C

<u>Wt Gain, mg/cm²</u>	<u>Oxidation Time, Hrs</u>	<u>Peak Location, cm⁻¹</u>				
0.232	95	1240 (1195)	1058 (950)	785	535	465
0.264	31	1240 (1190)	1035 (948)	780	525	460
0.320	72	1245 (1195)	(1070) 1015 (952)	787	535	460

Table 20

ASTM X-ray Data for TiSi₂*

<u>d, Å</u>	<u>I/I₁</u>	<u>hkl</u>	<u>2θ</u>
2.29	100	311	39.30
2.13	70	004	42.40
2.08	90	022	43.46
1.82	90	313	50.08
1.54	20	131	60.02
1.49	20	404,224	62.26
1.39	70	315	67.30
1.36	70	331	69.00
1.31	90	602	72.02

*Card number 10-225

Table 21
ASTM X-ray Data for TiSi*

<u>d</u>	<u>I/I₁</u>	<u>2θ</u>
2.906	20	30.74
2.716	20	32.95
2.660	70	33.66
2.409	100	37.29
2.316	70	38.85
2.172	80	41.54
1.983	60	45.72
1.950	80	46.53
1.842	10	49.44
1.805	80	50.52
1.736	20	52.68
1.690	10	54.23
1.607	20	57.28
1.575	10	58.56
1.542	70	59.94
1.517	40	61.03
1.428	80	65.28
1.399	30	66.81
1.339	70	70.24
1.318	40	71.50

*Card number 8-420

Table 22

ASTM X-ray Data for Ti_5Si_3^*

<u>d</u>	<u>1/l₁</u>	<u>hkl</u>	<u>2θ</u>
3.220	7	200	27.68
3.010	6	111	29.65
2.569	14	002	35.04
2.412	47	210	37.24
2.385	30	102	37.68
2.198	100	211	41.02
2.145	38	300	42.08
2.113	98	112	42.76
2.007	6	202	45.14
1.857	6	220	49.02
1.745	10	221	52.38
1.685	9	311	54.40
1.608	9	400	57.24
1.506	18	222	61.52
1.466	8	312	63.40
1.418	10	321	65.80
1.404	15	410	66.54
1.400	29	213	66.76
1.364	12	402	68.76
1.287	15	500	73.50

*Card number 8-41

Table 23

ASTM X-ray Data for Silicon*

<u>d</u>	<u>I/I₁</u>	<u>hkl</u>	<u>2θ</u>
3.138	100	111	28.42
1.920	60	220	47.30
1.638	35	311	56.19
1.357	8	400	69.16
1.246	13	331	76.38

*Card number 5-0565

Table 24

ASTM X-ray Data for TiO₂ (Rutile)*

<u>d</u>	<u>I/I₁</u>	<u>hkl</u>	<u>2θ</u>
3.245	100	110	27.46
2.489	41	101	36.05
2.297	7	200	39.18
2.188	22	111	41.22
2.054	9	210	44.04
1.687	50	211	54.33
1.624	16	220	56.62
1.480	8	002	62.72
1.453	6	310	64.02
1.360	16	301	68.98

*Card number 4-0551

Table 25

ASTM X-ray Data for α -Quartz*

<u>d</u>	<u>I/I₁</u>	<u>hkl</u>	<u>2θ</u>
4.26	35	100	20.83
3.343	100	101	26.64
2.458	12	110	36.52
2.282	12	102	39.46
2.237	6	111	40.28
2.128	9	200	42.44
1.980	6	201	45.78
1.817	17	112	50.16
1.801	<1	003	50.64
1.672	7	202	54.86
1.659	3	103	55.33
1.608	<1	210	57.24
1.541	15	211	59.98
1.453	3	113	64.02
1.418	<1	300	65.80
1.382	7	212	67.74
1.375	11	203	68.14
1.372	9	301	68.30
1.288	3	104	73.46

*Card number 5-0490

Table 26

ASTM X-ray Data for α -Cristobalite*

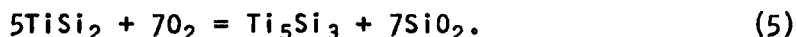
<u>d</u>	<u>I/I₁</u>	<u>hkl</u>	<u>2θ</u>
4.04	100	101	21.98
3.14	12	111	28.40
2.85	14	102	31.36
2.49	18	200	36.04
2.47	6	112	36.34

*Card number 11-695

Mixtures of TiO_2 and SiO_2 were prepared to determine the minimum amount of TiO_2 that could be observed in the X-ray scan. A summary of the results is shown in Table 27. These data indicate that the minimum amount of TiO_2 which can be detected is approximately 1 percent. Calibration curves using the intensity and intensity ratio were prepared to determine the TiO_2 concentration of heat-treated specimens.

3. X-ray Depth of Penetration

If a lower silicide is formed at 600°C , the probable reaction would be



In the present study, a typical weight gain after 100 hours at 600°C is approximately 0.1 mg/cm^2 . If the above reaction is assumed to be correct, an SiO_2 film about $9000 \text{ \AA}$ thick would be formed corresponding to this weight gain. If the lower silicide forms in a layer beneath the oxide, its thickness would be approximately $3000\text{-}4000 \text{ \AA}$. In order to detect the Ti_5Si_3 , it is necessary for the X-ray to penetrate the oxide film and the Ti_5Si_3 layer. If the X-ray goes considerably further into the TiSi_2 below, the Ti_5Si_3 may not be observed.

Most metallic materials strongly absorb X-rays with the result that the incident beam is reduced almost to zero in a very short distance below the surface. The diffracted beams are typical then of a thin surface layer. The intensity of the incident beam decreases exponentially with distance below the surface. This can be represented by

$$I = I_0 \exp(-\mu x) \quad (6)$$

where μ is the linear absorption coefficient, x the depth of penetration and I and I_0 the intensity of the diffracted and incident beams,

Table 27

Sensitivity of X-ray Method

TiO ₂ Conc., Wt %	Peak Position (Intensity)		Intensity Ratio TiO ₂ /SiO ₂
	TiO ₂	SiO ₂	
2.35	27.51 (4.4)	20.88 (40)	0.110
2.35	27.55 (4.7)	20.96 (36)	0.131
4.04	27.52 (7.0)	20.91 (31)	0.226
4.04	27.48 (5.0)	20.95 (24)	0.208
8.10	27.50 (9.6)	20.90 (34)	0.283
8.10	27.45 (10)	20.89 (40)	0.250
0.88	(0)	20.95 (38)	0
6.18	27.51 (9)	20.89 (36)	0.250
10.2	27.46 (12)	20.95 (35)	0.343
9.32	27.50 (10)	20.90 (26)	0.385

$$2\theta = 27.50 \pm 0.03 \quad 20.92 \pm 0.03$$

$$d = 3.241 \pm 0.004 \quad 4.24 \pm 0.01$$

respectively. The observed dissipation of the X-ray beam is due to scattering and absorption. Scattering is usually only significant for the very light elements.

Cullity (54) gives as a useful relationship for approximating the effective depth of penetration of X-rays when using a diffractometer

$$G_x = (1 - e^{-2\mu x / \sin\theta}) \quad (7)$$

where G_x is the fraction of the total diffracted intensity supplied by a layer of thickness x , and θ the angle of incidence. In order to make use of equation (7), it is necessary to know the linear absorption coefficient, μ , which is dependent on the material considered, its density and the wavelength of the X-rays. Cullity has tabulated data on μ/ρ and gives values of 60.3 for silicon, 204 for titanium and 12.7 cm²/gm for oxygen for CuK α radiation with $\lambda = 1.542 \text{ \AA}$.

The mass absorption coefficient of a substance containing more than one element can be estimated from the following relationship

$$\mu/\rho = W_1(\mu/\rho)_1 + W_2(\mu/\rho)_2 + \dots \quad (8)$$

where W_1 is equal to the elemental weight fraction. For the materials in this study, the following values of μ/ρ were calculated.

<u>Material</u>	<u>μ/ρ, cm²/gm</u>	<u>μ, cm²</u>
TiSi ₂	126	30.5
Ti ₅ Si ₃	167	38.7
SiO ₂	35.0	16.7
TiO ₂	127	
2SiO ₂ -TiO ₂	71.7	

Using equation (7) with $\mu = 38.7 \text{ cm}^{-1}$ and $2\theta = 40^\circ$, the position of the major Ti₅Si₃ peaks, a value of 0.0113 is obtained for the fraction

of the total energy diffracted by a 5000 Å thick Ti_5Si_3 film. This calculation indicates that almost all the diffracted energy is attributable to the TiSi_2 substrate. It is quite likely that a Ti_5Si_3 layer of 5000 Å would not be observed using the diffraction method.

C. TiSi_2 Oxidation Data

Figures 26-30 show additional weight gain data for the oxidation of TiSi_2 . Figures 27 and 28 are typical of the data obtained with samples which had a moderate number of holes in the surface.

D. TiSi and Ti_5Si_3 Data

Figure 31 shows X^2 versus t for the TiSi wafers oxidized at 1000°C. Figure 32 is similar data for Ti_5Si_3 . Figure 33 is also for Ti_5Si_3 .

E. TiO_2 - SiO_2 Solubility and Glass Formation

A number of 0.5 inch diameter wafers containing 10.2 percent Cabot TiO_2 and 89.8 percent Fisher Scientific α -quartz were fired in air at elevated temperatures. At 600, 800 and 1200°C for one hour, and 1000°C for 16.5 hours, the original α -quartz and rutile were still present. At 1400°C for two hours, part of the α -quartz had inverted to α -cristobalite while the amount of rutile observed in the X-ray pattern appeared unchanged. These data confirm the results of Ricker and Hummel (21) where it was found that long reaction times of at least 30 hours were required to achieve solubility at temperatures below 1400°C.

The results of the heat treatment carried out in vacuum are shown in Table 28. At 1200°C, 0.5 minutes is sufficient time to result in the disappearance of the characteristic rutile peaks in a sample originally containing 10 percent TiO_2 . After firing, the top surface and sides of the sample were, in most cases, light blue while the bottom

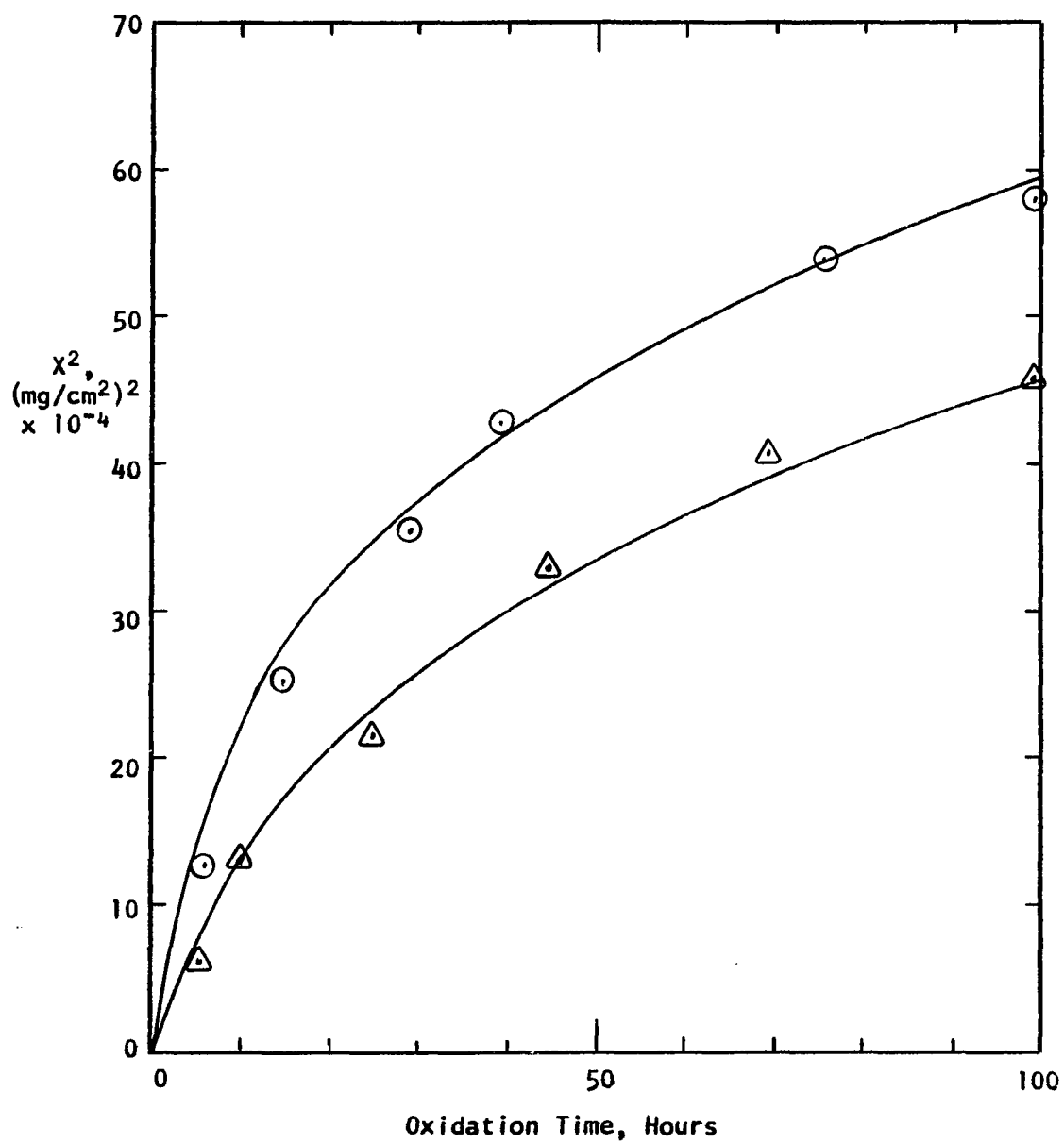


Figure 26. X^2 versus t for TiSi_2 Oxidized at 800°C

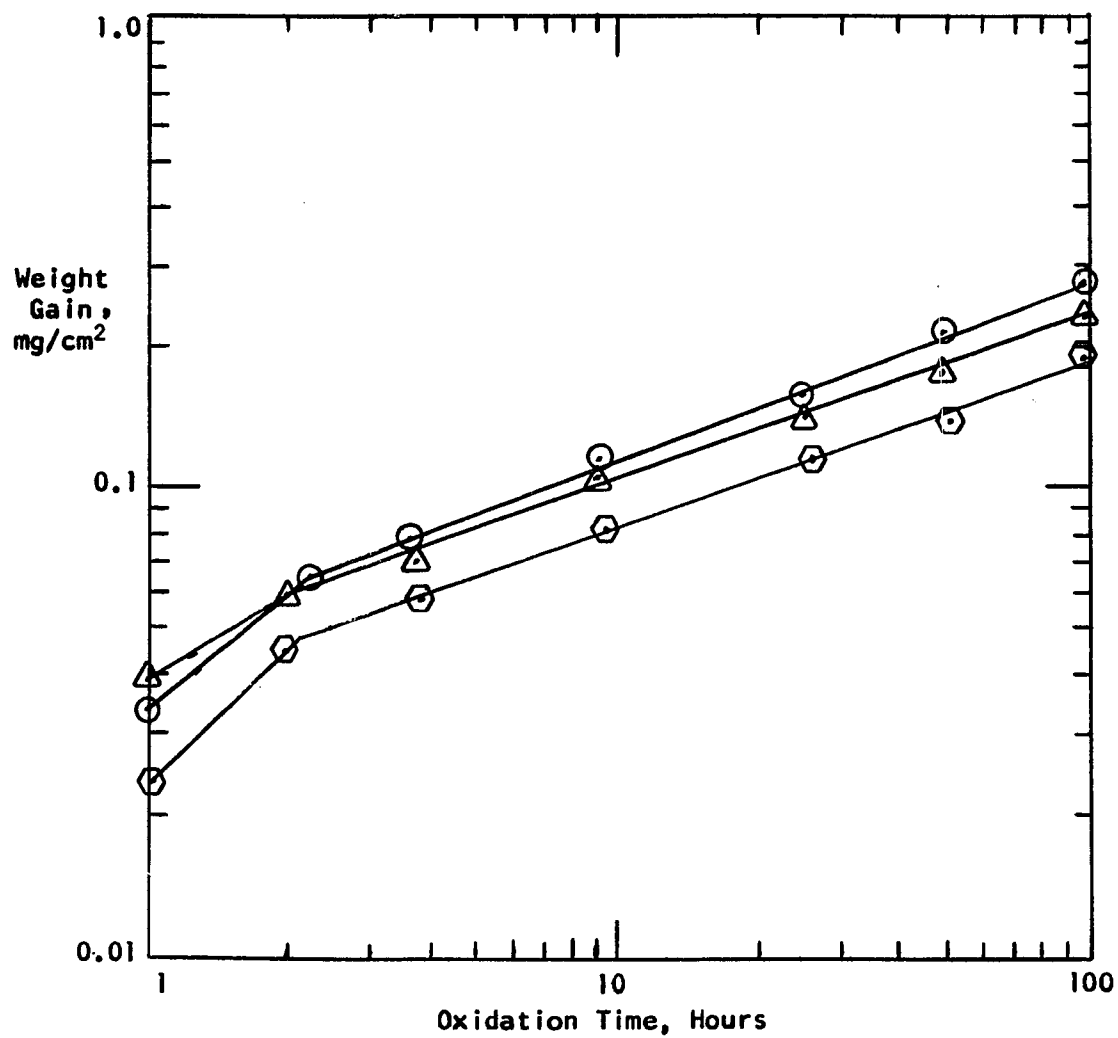


Figure 27. Weight Gain Data for TiSi_2 Samples with a Moderate Number of Holes Oxidized at 1000°C

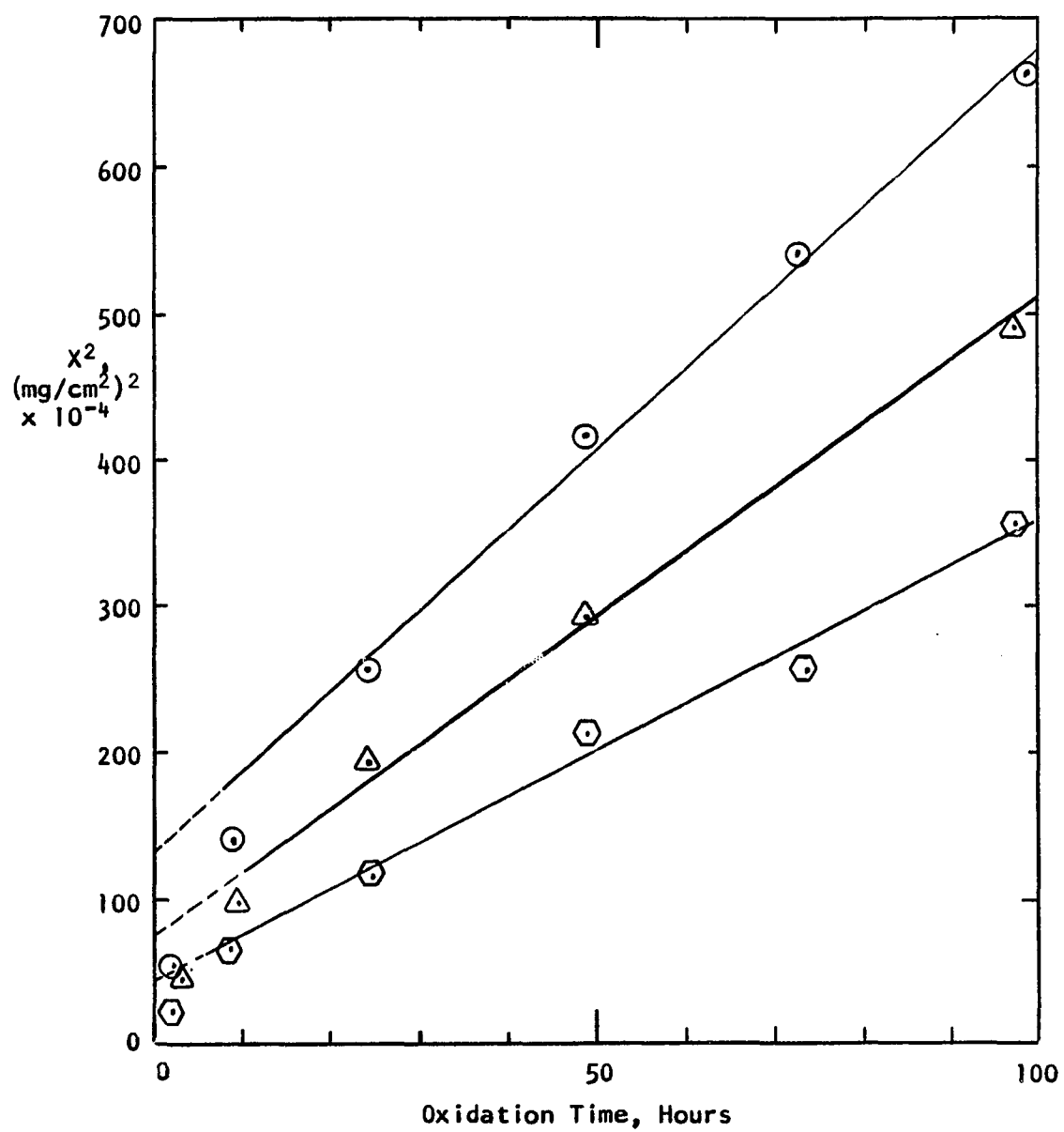


Figure 28. X^2 versus t for Data of Figure 27

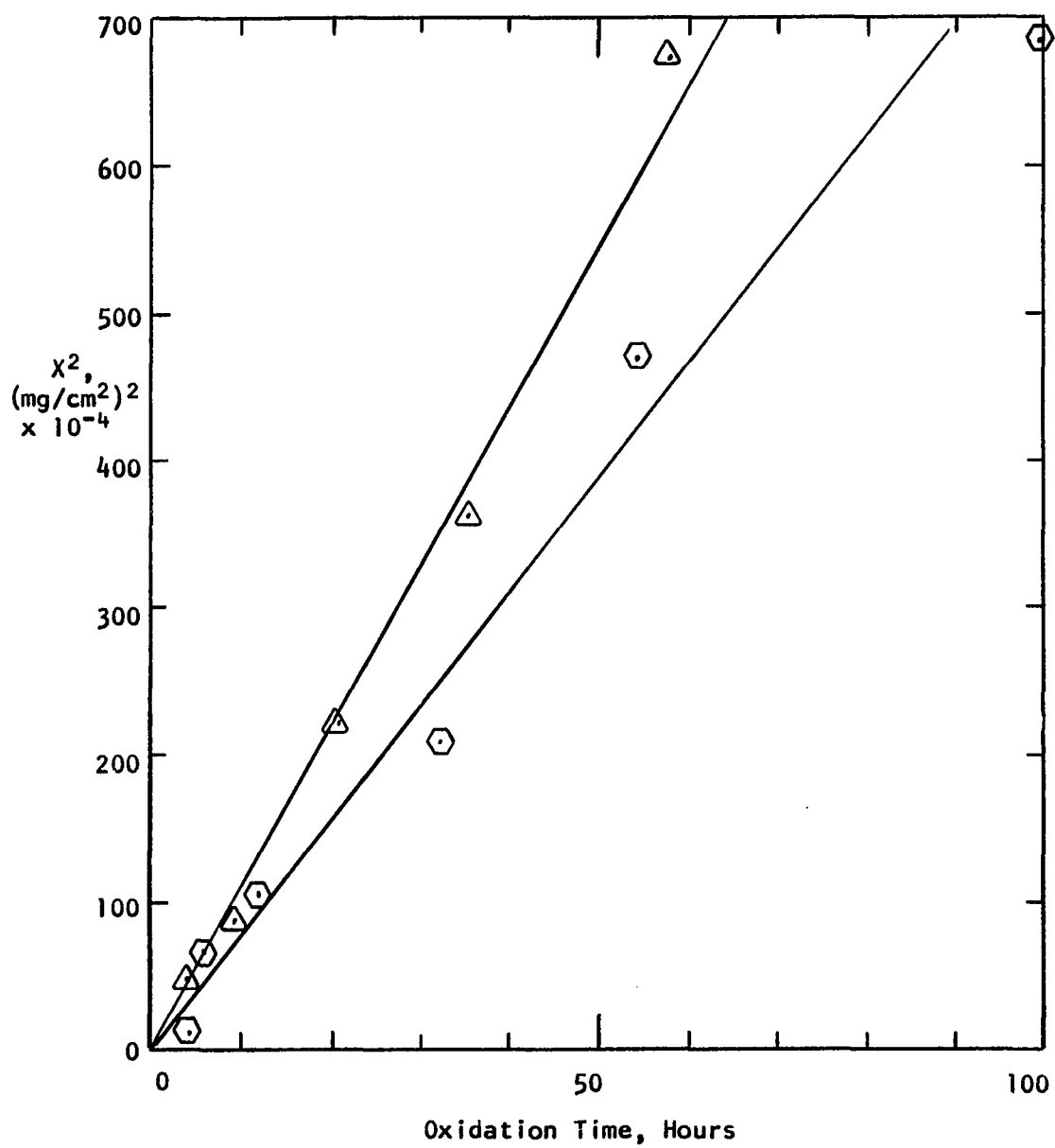


Figure 29. x^2 versus t for TiSi_2 Oxidized at 1200°C

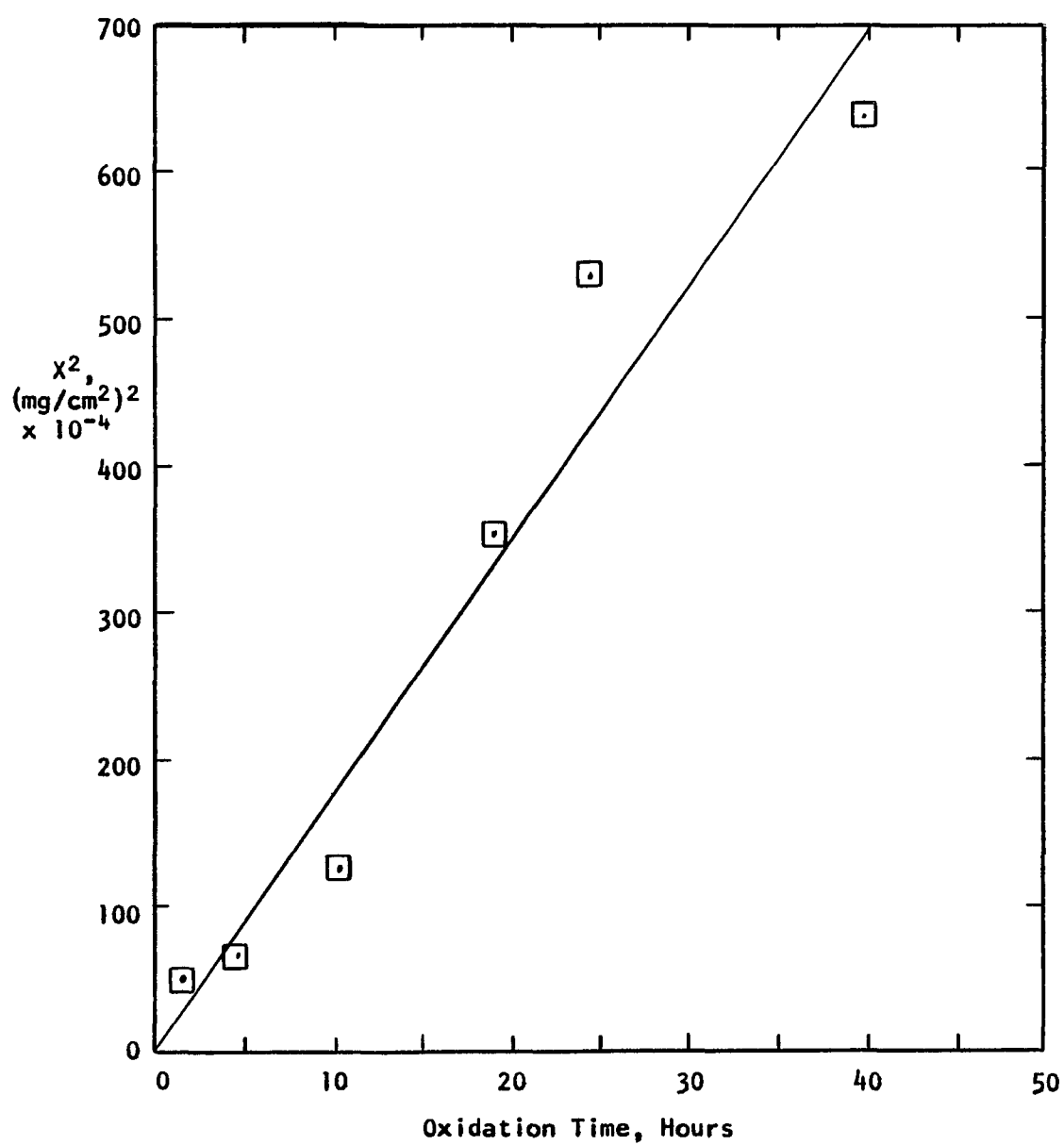


Figure 30. x^2 versus t for TiSi_2 Oxidized at 1300°C

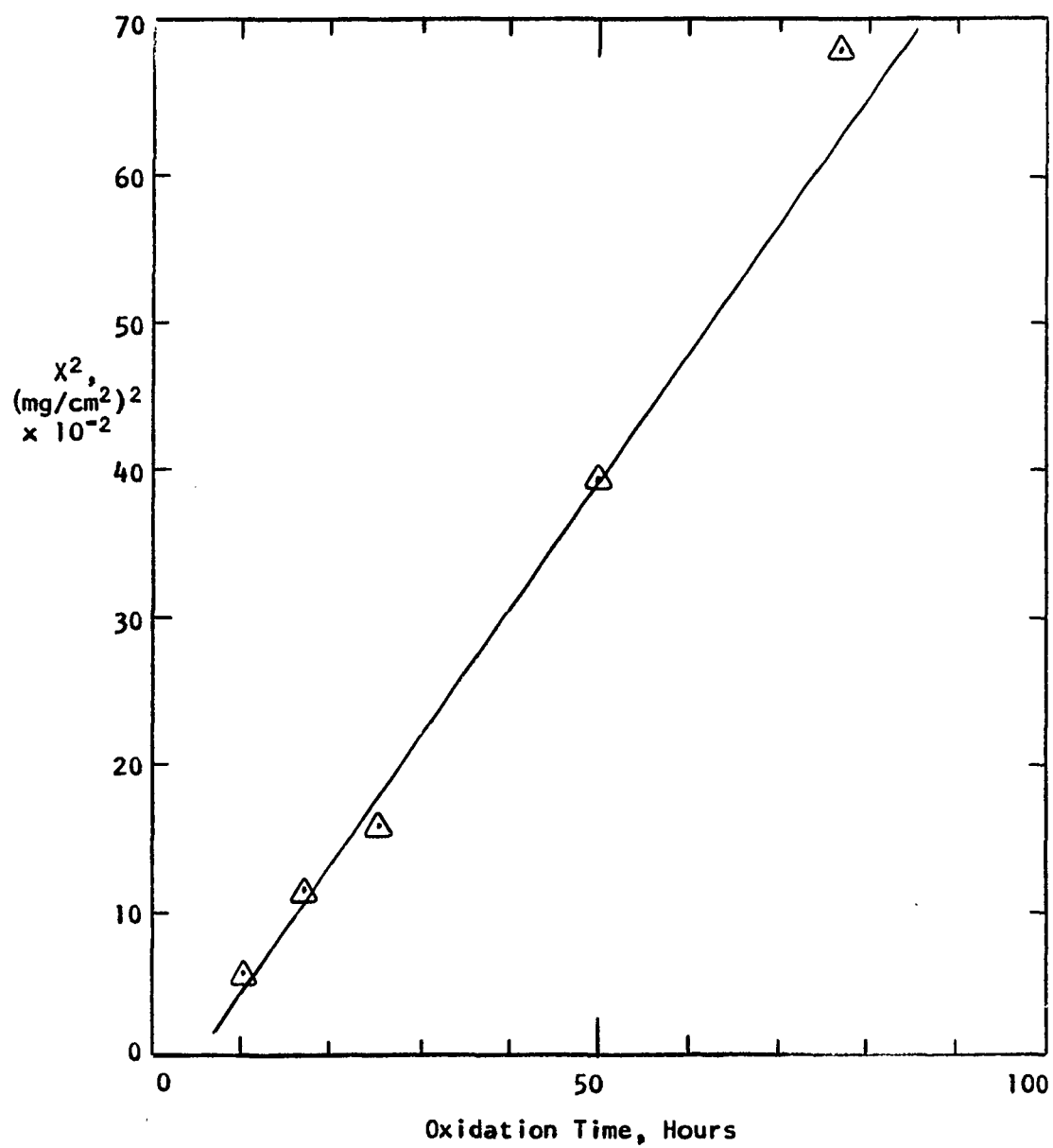


Figure 31. X^2 versus for TiSi oxidized at 1000°C

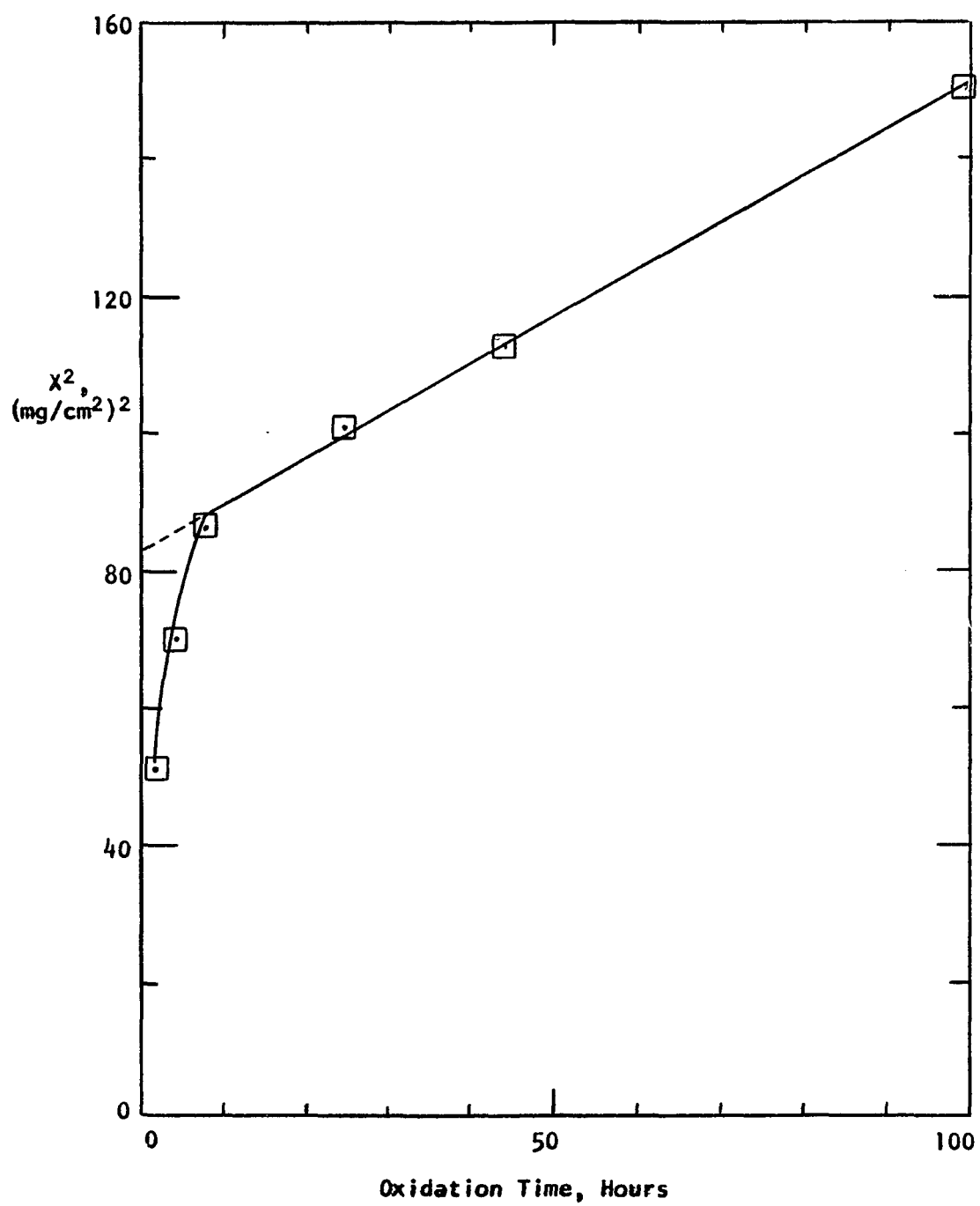


Figure 32. x^2 versus t for Ti_5Si_3 Oxidized at $1000^\circ C$

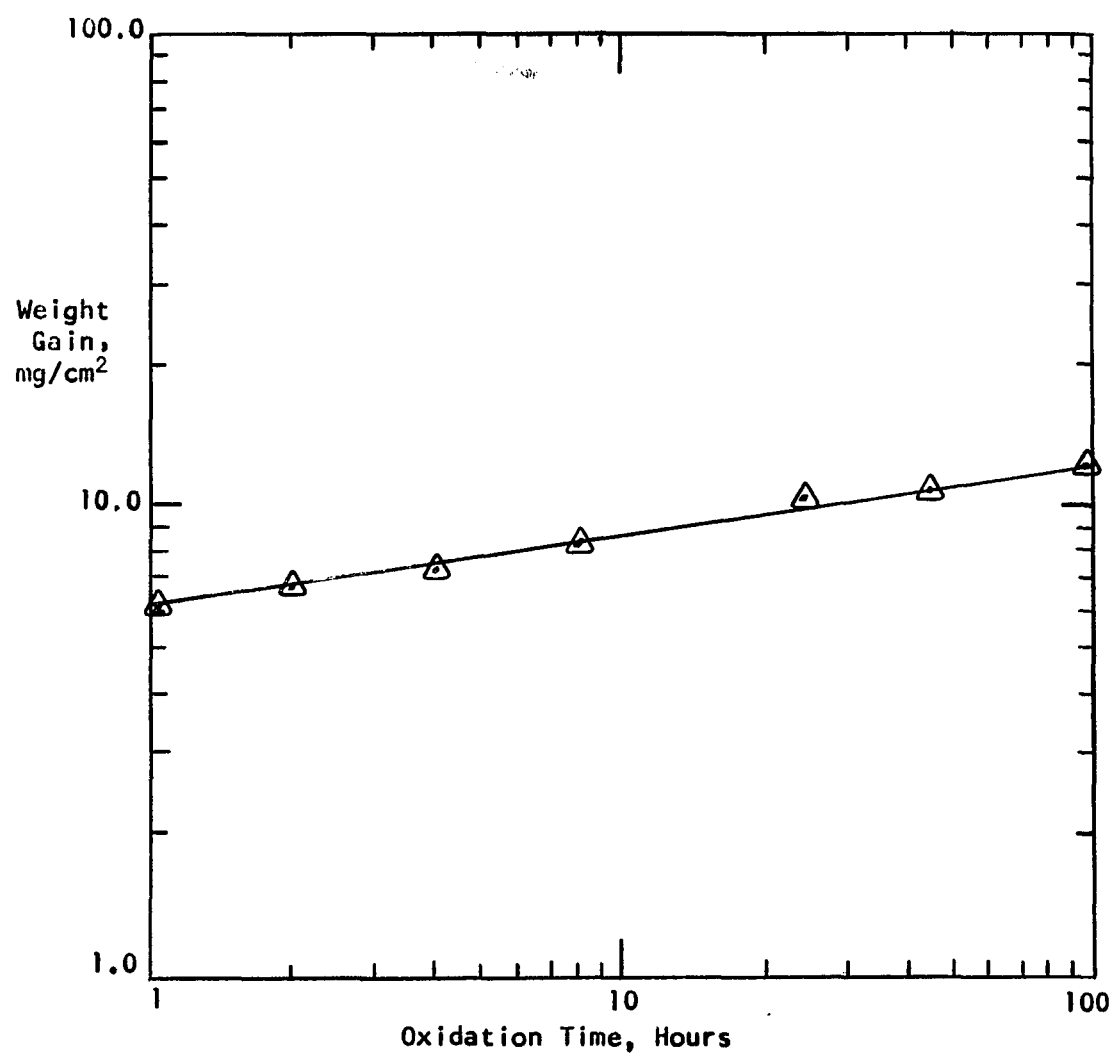


Figure 33. Oxidation Weight Gain Data for Ti_5Si_3

Table 28

TiO₂-SiO₂ Vacuum Heat Treatment Data

Run No	TiO ₂ Conc, Wt %	Temp, °C	Pressure x 10 ⁻⁴ , Torr	Time, Min	SiO ₂ Source	Analysis	
						X-ray	IR
500	9.7	1200	1	0.5	GE	Q	Q
513	10.2	1225	0.3	30	Fisher	Q	
514A	8.65	1250	1	15	GE	Q	
506A	10.2 ^a	1570	1	15	Fisher	R(t) Q(t)	A, 935 cm ⁻¹
506B	10.2 ^a	1615	1	15	Fisher		A, 935 cm ⁻¹
501	20.3 ^b	1545	1	0.5	GE	Q, R	
501(1)	20.3 ^b	1470	1	15	GE	Q, LC, R	
501(2)	20.3 ^b	1475	1	30	GE	Q, LC, R	A, Q, 945, 615 cm ⁻¹
504	22.5 ^c	1650	1	15	GE		
502	30.2 ^c	1615	1	0.5	GE		
505	30.4 ^d	1650	1	15	GE	R	A, 930 cm ⁻¹

Q - α-quartz

R - rutile

LC - α-cristobalite

A - amorphous SiO₂

(t) - trace

a - sample coalesced

b - same sample

c - sample started to melt

d - melted

was dark blue. The density of the sample had increased considerably indicating sintering. X-ray analysis of the light blue surface indicated about 2-3 percent crystalline TiO_2 . The light blue color is confined to the region near the surface. Light abrasion with 500 grade silicon carbide paper revealed the dark blue interior. X-ray analysis of the dark blue region showed no crystalline TiO_2 . The infrared spectrum was similar to that of the pure silica. No shifts were observed in the absorption maximas.

Data are also given in Table 28 for firings made around the eutectic temperature of 1540°C . A sample containing 10.2 percent TiO_2 was heated at 1570°C for 15 minutes at 10^{-4} Torr. The sample had coalesced but had not bonded to the alumina dish. X-ray analysis indicated that the material was amorphous with trace amounts of α -quartz and rutile. As shown below, the peaks were shifted to lower angles, i.e., greater "d" values.

Observed		Standard		Identification
2 θ	d	2 θ	d	
20.7	4.29	20.83	4.26	α -quartz
26.50	3.36	26.64	3.34	α -quartz
27.25	3.27	27.46	3.25	rutile
49.9	1.83	50.16	1.82	α -quartz
54.1	1.69	54.33	1.69	rutile

The infrared spectrum for this sample is similar to that of amorphous SiO_2 with one major exception. A new absorption peak is observed at 935 cm^{-1} . In addition, the shoulder on the 1075 cm^{-1} peak appears to have shifted from the 1170 cm^{-1} in pure silica to 1220 cm^{-1} . A sample fired at 1615°C gave essentially the same infrared spectrum.

When the TiO_2 concentration was increased to 20.3 percent and fired at 1545°C for 0.5 minutes, a blue, glossy material with rounded edges formed. X-ray analysis indicated a considerably reduced amount of α -quartz and considerable TiO_2 . X-ray analysis after further heating at 1470°C for 30 minutes indicated α -cristobalite, α -quartz and considerable TiO_2 . The infrared spectrum showed vitreous silica, some α -quartz with additional peaks at 945 and 615, a small peak at 690 and a shoulder at 775 cm^{-1} . A sample containing 22.5 percent TiO_2 fired at 1650°C melted and bonded to the alumina.

With 30.4 percent TiO_2 fired at 1650°C for 15 minutes, melting and bonding to the alumina occurred. X-ray analysis indicated only TiO_2 . The infrared spectrum indicated vitreous SiO_2 with an additional peak at 930 cm^{-1} . The 930 cm^{-1} absorption is more intense and broader than at the lower TiO_2 concentrations.

A number of samples were annealed in air at low temperatures after having been heated in vacuum. Wafers containing 9.32 percent TiO_2 were heated at 1200°C for 15 minutes and 8×10^{-5} Torr. X-ray analysis of the surface indicated approximately 2 percent TiO_2 . After annealing in air at 400°C for 70 hours, the crystalline TiO_2 concentration on the surface appeared to have increased to 3 percent. This surface was ground off and X-ray analysis of the underlying surface indicated about 3-4 percent TiO_2 . After reheating for an additional 72 hours, X-ray analysis indicated 5 percent TiO_2 on the surface. Further heat treatment is summarized on the following page.

<u>Time, Hours</u>	<u>TiO₂, %</u>
0	2
70	3
70 (ground)	3-4
142	5

After this treatment, the sample was pale blue.

Another sample was heated at 700°C in air for 0.25 hours. X-ray analysis indicated 5 percent TiO₂ or about half that present in the original charge. The sample was white after annealing.

The weight change of a sample containing 8.10 percent TiO₂ during cycling from air to vacuum heating was recorded using an analytical balance. After 1 hour in air at 1200°C, a weight loss of 0.028 percent (0.2 mg from a 708.5 mg sample) was observed. Heating in a vacuum of 10⁻⁴ Torr also at 1200°C gave another 0.028 percent weight loss. After reheating in air at 1200°C for 0.5 hours, the white color returned. No weight change was observed. X-ray analysis indicated that all the crystalline TiO₂ in the sample was again present.

A number of runs were also made in the high titania region of the phase diagram. A sample of pure Cabot TiO₂ was fired at 1200°C for 15 and 45 minutes in a vacuum of 8 x 10⁻⁵ Torr. The sintered sample was blue and had a density of 84 percent of the theoretical value. X-ray analysis of the unfired and fired samples indicated no change in either peak position or intensity.

A sample containing 85.3 percent TiO₂ and 14.7 percent α-quartz was also sintered at 1200°C for 15 minutes and 8 x 10⁻⁵ Torr. The

The wafer was blue after firing. The α -quartz and TiO_2 peak positions in the X-ray pattern were essentially unchanged. The peak intensities were also unchanged, except for the TiO_2 peak at $2\theta = 27.5^\circ$ which decreased about 25 percent.

The data obtained in this study indicate that when a mixture of 10 percent TiO_2 and 90 percent SiO_2 is heated at $700\text{--}1300^\circ\text{C}$ in vacuum for short times, the sample turns blue and the X-ray peaks characteristic of crystalline TiO_2 disappear. The crystalline SiO_2 lines are retained. The infrared spectrum of the fired product is typical of the charged silica. When reheated in air below 1300°C , the sample returns to its original white color and the TiO_2 reappears.

The weight change data obtained indicate that no major titanium or oxygen losses had occurred. For a typical sample, the following tabulation shows the weight losses that would have been expected if the various changes indicated had taken place.

<u>Change</u>	<u>Weight Loss, mg</u>
TiO_2 evaporates	57.4
Ti evaporates	34.4
TiO formed	11.5
$\text{TiO}_{1.95}$ formed	0.58
$\text{TiO}_{1.98}$ formed	0.23

If the observed weight loss of 0.2 mg is significant, then a defect structure could have formed. It is known that SiO_2 and TiO_2 form defect structured when heated in vacuum. Ewes and Youell (56) have studied the defects formed in SiO_2 at 10^{-4} Torr and 1250°C . They indicate a 0.01 percent oxygen deficit occurring at these conditions.

In air at 1250°C, no weight change is observed. TiO_2 also forms oxygen defects (57) when heated above 800°C in reduced oxygen pressures. It is highly unlikely that the presence of the defects could cause both the X-ray and infrared TiO_2 characterizations to disappear.

At temperatures slightly below the eutectic, the TiO_2 peaks in the X-ray are considerably diminished while a new absorption is observed in the infrared at 935 cm^{-1} . In addition, a small absorption characteristic of TiO_2 is observed at 690 cm^{-1} .

If a solid solution were formed, a Ti-O-Si vibration would be expected. Zeitler and Brown (44) have reported results on the infrared spectra of organic-titanium-silicon compounds. Data pertinent to this study are shown below.

<u>Compound</u>	<u>Wave No., cm^{-1}</u>	<u>Interpretation</u>	<u>Strength</u>
$[(\text{C}_6\text{H}_5)_3\text{SiO}]_4\text{Ti}$	925	Ti-O-Si	very strong
$[(\text{CH}_3)_3\text{SiO}]_4\text{Ti}$	1057	Si-O	moderate
	919	Ti-O-Si	very strong
$[(\text{C}_6\text{H}_5)_3\text{SiO}]_4\text{Ti}$	1082	Si-O-Si	strong

The vibration that the authors attribute to a Ti-O-Si bond is given as $920\text{-}925\text{ cm}^{-1}$. This value is $10\text{-}20\text{ cm}^{-1}$ lower than the unidentified peaks obtained in the present work. Zeitler and Brown's data show the Si-O bond stretching vibration at $1060\text{-}1080\text{ cm}^{-1}$. These value are also $10\text{-}20\text{ cm}^{-1}$ lower than that observed for Si-O bonds in the present work. It, therefore, appears reasonable to assign the vibration at 935 cm^{-1} in the present study to a Ti-O-Si vibration.

The silica interatomic distances do not indicate solid solution. If a solid solution were formed by the substitution of the larger

titanium atom for the silicon atom in the α -quartz lattice, one might expect a change in the lattice parameter. The X-ray data in this study show no change in the "d" values of the silica when the crystalline TiO_2 lines have disappeared. Some of the air firing data reported by Ricker and Hummel (21) are shown in Table 29. These results also indicate no variation in the "d" values for rutile when partial solution occurs. For high TiO_2 concentrations, their "d" values for both TiO_2 and SiO_2 are greater.

The constancy of the lattice parameter may not be unreasonable. At the 10 percent level, approximately one out of every 20 silicon atoms would be replaced by a titanium atom. This low concentration could easily be missed with the X-ray technique used.

The mechanism for the effect of vacuum is not clear. The presence of defects at the low pressure would considerably increase the diffusivities of the various species. In addition, a more open structure would be formed which might accommodate the titanium ion more readily. While this might explain the results at 1500°C , it does not clarify the data at 1200°C , particularly the disappearance and re-appearance of the TiO_2 lines in the X-ray when cycling from vacuum to air.

F. Thermodynamic Calculations

Based on the results of other silicide studies, the possible reactions for the oxidation of TiSi_2 are:

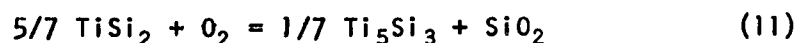
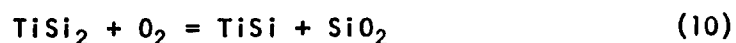
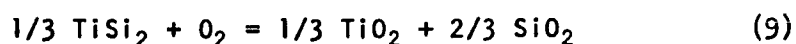


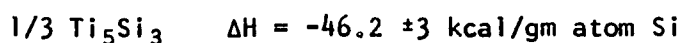
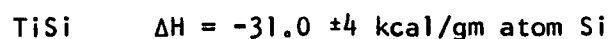
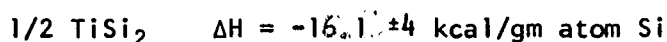
Table 29

Lattice Parameter Variation in the TiO₂-SiO₂ System
After Heat Treatment at Elevated Temperatures (21)

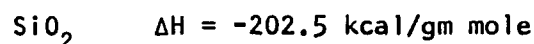
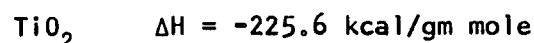
TiO ₂ Conc, Wt %	Temp, °C	Time, Hrs	<u>"d" Values</u>						
0 ^a	1500	10	4.01	3.11	2.83	2.47	1.92	1.86	1.61
10.5	1500	10	4.01	3.11	2.84	2.47		1.87	1.61
20.0	1500	10	4.01	3.12	2.85	2.48			1.62
92.0	1500	10	4.08						
0			4.10			2.53			1.64
10.5	1625	1	4.10			2.52			1.64
20.0	1625	1	4.10			2.53			
57	1625	1	4.08						

^a - High cristobalite

In order to determine which reaction is predicted thermodynamically, the free energy of formation is needed. Since free energy or entropy of formation data are not available for the silicides, it is necessary to use the heat of formation data in the calculation. Searcy (19), after reviewing the earlier literature studies, cites the following "preferred" values for the heat of formation of the titanium silicides at 298°K:



The heat of formation data for the oxides are reported as (58):



Using the enthalpy data for the silicides and the oxides, the following enthalpy changes were calculated at 25°C for the above reactions:

$$(9) \quad \Delta H_F = -199.5 \text{ kcal/mole O}_2$$

$$(10) \quad \Delta H_F = -201.3 \text{ kcal/mole O}_2$$

$$(11) \quad \Delta H_F = -199.3 \text{ kcal/mole O}_2$$

The error involved in using heat of formation data in place of free energy data is probably small. The free energy of formation is less than the heat of formation by the product of the absolute temperature and the entropy of formation. If the actual entropy change is about 3 cal/deg at 1500°K, the actual free energy would be 4.5 kcal more negative than when the ΔS is assumed to be zero.

XI. BIBLIOGRAPHY

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