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On the Atmospheric Oxidation of Pure and Siliconized Ta Metal Sheets at 1000°C

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Abstract

With a pure silicon vapor technique Ta sheets were siliconized in an evacuated quartz ampoule up to 49 hr at 1000°C, and then these siliconized sheets as well as untreated ones were oxidized at 1000°C for 15 min in an atmospheric air in order to determine the resistance of siliconized Ta metal against oxidation. Severe oxidation of pure Ta sheets almost prevented by using this method under the above-metioned conditions. Next, the mechanism of this protection process of siliconizing was discussed.

1. Introduction

Investigation and development of new metallic materials aganist the high-temperature oxidation attack are in strongly demand, since the environment in which metallic materials are used has recently become increasingly detrimental.

There are various methods to improve the anti-corrosion property of refractory metals. The practice of surface coating with vapored metals has drawn special attention as an effective method. For example Inconel alloys now widely used for turbine blades are at times coated with the anti-corrosion metal by a vapor-diffusion method, resulting in a satisfactory modification of the oxidation resistance.

From this point of view, the present investigatin was carried out to examine in what manner a siliconized Ta sheet shows better resistance against the oxidation attack than that of an untreated Ta sheet, because pure Ta metal fails easily in atmospheric environment above 1000°C in spite of its excellent mechanical properties at elevated temperatures and furthermore, the vapor pressure of Si is relatively high and easily produced.

So far the oxidation of pure Ta metal has been investigated by Peterson et al.[1], Gulbransen and Andrew[2], Bakish[3], Michael[4], and Albrecht et al[5]. Recently, there is a detailed report by Dooley et al.[6,7] on the oxidized structure of single and polycrystalline Ta metals. Generally, the oxidation of polycrystalline Ta is found to obey a logarithmic corrosion rate law below 500°C and a parabolic rate law in a range of 500 to 1000°C, and it is oxidized linearly above 1000°C.

The effect of alloying elements for Ta metal against oxidation was investigated comprehensively by Kloop et al.[8], who showed good improvment of anti-oxidation properties in the order of Ni, Mo, Cr, and Si in atmospheric oxidation for 1 hr at 1200°C. From those results, if Si could penetrate into Ta metal through its surface, the treated metal would show good resistance in air-oxidation at elevated temperatures. Consequently, siliconizing of Ta sheets in Si vapor will be probably

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accomplished relatively easily and an excellent resistance of the metal aginst the oxidation attack may well be obtained.

2. Experimetal procedures

Test pieces for the present experiment were prepared from sheets (0.3 mm thick) made by Van steel Co., U. S. A. These were cut down to a size of about 10×10 mm and annealed at 1000°C for 1 hr in a quartz ampoule evacuated of air up to 4×10^{-6} mmHg and then their surfaces were polished up to #1000 emery paper followed by washing and degreasing.

Such test pieces were capsuled once more in a quartz tube at an order of 10^{-6} mmHg with pure Si powder (−200 mesh) prepared by The Shin-etsu Chemical Industry Co. Ltd. and diffusion-annealed in an electric furnace as shown in Fig. 1 for various lengths of time at 1000°C.

Table 1 shows the details of this siliconizing experiment, listing the purities and vapor pressures of both metals. The siliconized metal sheets were then oxidized in the apparatus shown in Fig. 2, in which a test piece was hung in a vertical quartz tube through which air was allowed to flow up at a rate of 100 cc/min. This flow rate of air was determined after comparing its effect on the oxidation rate of pure Ta sheets. Moreover, the variation of oxidation rate was checked with or without desiccating the flowing air and the effect of such treatment on the corrosion was found to be much less.

These oxidized test pieces were observed microscopically and diffractometrically and also the sectioned parts were checked by means of an elecron probe microanalyzer (EPMA).

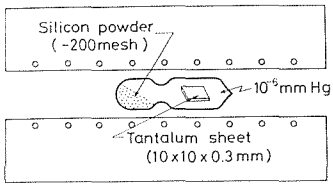


Fig. 1 Schematic presentation of siliconizing ampoule and its furnace

Table 1 Test piece and siliconizing condition

	Time (hour)
1000°C	1 4 9 16 25 36 49

SILICON	TANTALUM
99.999 % Si	99.9 % Ta min. 0.03 % Fe max. 0.03 % C max.
VAPOR PRESSURE, 1000°C	
10^{-5} mmHg	10^{-21} mmHg,
MELTING TEMPERATURE	
1410 °C	2996 °C

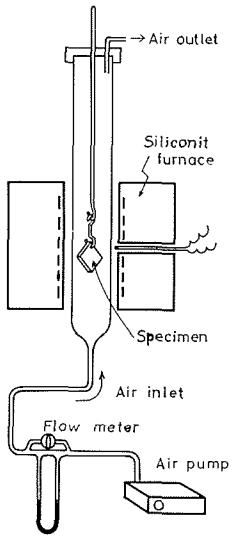


Fig. 2 Schematic presentation of oxidation apparatus

3. Results

3.1 Oxidation of pure Ta sheet

On account of the shape of a test piece oxidation over a long period failed owing to its descent. Hence the oxidation test was carried out within 15 min at 1000°C. The results obtained for the change in weight with the square root of corrosion time was shown in Fig. 3 (a) in which the oxidation seems to obey a parabolic rate law in general, showing only a slight deviation from that law. This behavior is more clearly indicated by a log-log expression shown in Fig. 3 (b), which shows that the relation of weight gain (ΔW) with time (t); $\Delta W = kt^n$ holds with the value of $n=0.64$, because it is mainly due to the abnormal oxidation at the corners of the test piece as will be stated later. From the experimental results the metal shows a weight increase of about 23.5 mg/cm² in 15 min at 1000°C and the rate constant k in this case is abut 4.0 (mg/cm² min$^{1/2}$).

The surface of oxidized sheet was pale grey and was firmly adhered to the substrate, but the oxide scales showed some cracks from which white oxide was

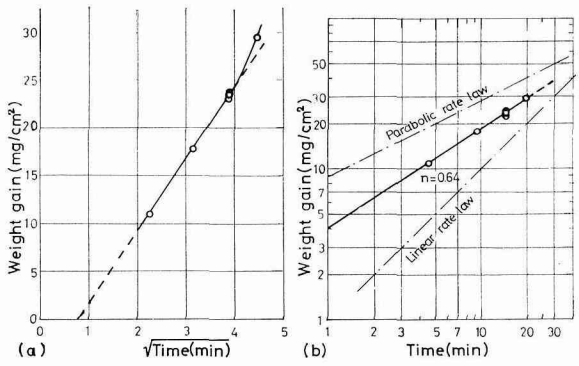


Fig. 3 Weight gain vs. time

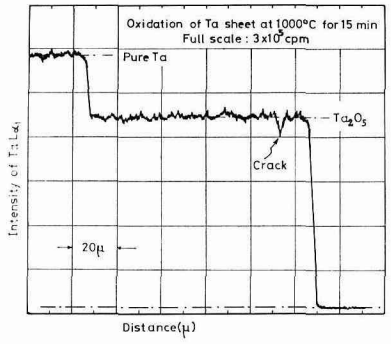


Fig. 4 EPMA profile from oxidized Ta sheet

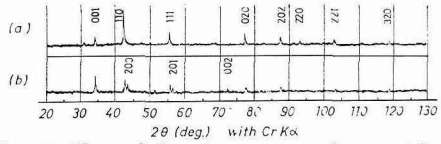


Fig. 5 X-ray diffraction patterns from oxidized Ta (Ta_2O_5)
(a); Surface, (b): White oxide powder

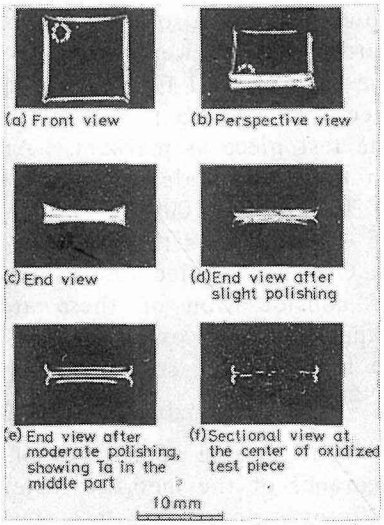


Photo. 1 External and sectional views of oxidized Ta sheet

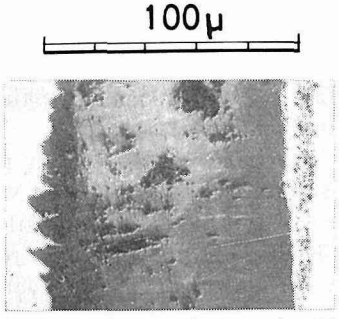


Photo. 2 Sectional view of oxide with markers on its surface.
left: Ta, right: plated Ni

seen extruding. The stripes seen on the oxidized surface may be scratches from the polishing abrasion. At the corners of the test piece abnormal behavior was seen. Namely, the above-stated white oxide crystals extruded and appeared curled up as seen in Photo. 1. Detailed inspections showed that the corners had no scales as pointed out previously by Dooly et al[7].

The microstructure of the sectioned part of oxidized metals was shown in Photo. 2. The oxide appears dark grey, and the metal/oxide interface was not flat, showing an irregular oxidation. This fact would be attributable to the preferential oxidation at the grain boundary of the metal substrate. An EPMA result showed the distribution of Ta in the section as seen in Fig. 4 for example, from which the scales seemed to be Ta_2O_5 (identified later) equally throughout the oxide scale. Such scales are very hard and are adhered to the substrate as stated above, so that the removal of it from the metal substrate was very difficult.

The removal was not done to check the oxide crystal by means of an x-ray diffractometer.

The x-ray diffraction of the oxidized surface made for various oxidation times all indicate the same crystal patterns, and that from the white oxide crystal powder shows also the same crystal, although it contained some other diffraction patterns which were probably due to the difference between the orientations of the same crystal (see Fig. 5 (a) and (b)). In order to investigate the oxidation mechanism of Ta metal, alumina particles (0.5 $\mu\phi$) were placed on the surface of the test piece as markers. After the oxidation the almina maker was still found on the oxide scale of Ta sheet, as seen in Photo. 2. Consequently, the oxidation of Ta metal at 1000°C was concluded to be performed by only an inward diffusion of oxygen atoms through the oxide (Ta_2O_5). According to Kubaschewski et al.[9] Ta_2O_5 was classified into a metal-excess type (n-type semiconductor), but as a result of consideration of these atomic sizes and observation of the marker in this experiment this oxide may be rather regarded as an anion-deficit n-type at 1000°C, so that movable species seems to be oxyen atoms alone rather than Ta atoms.

3.2 Siliconizing of pure Ta sheet

The surface appearance of siliconized Ta sheets is dark grey with a disappearance of the metallic luster observed before the treatment, but there was no difference among the test pieces for various treating intervals.

The results from the x-ray diffraction analysis for each test piece are shown in Fig. 6, in which x-ray patterns on its surface for a short time (4hr) are almost the same ($TaSi_2$) as those for a long time (49hr) except the former shows other peaks. These peaks were clearly identified as Ta_5Si_3, so that the compound formed for a short time may be regarded to be in a transient phase. Therefore, the surface seems to consist mainly of the same compound in spite of the various treating intervals.

The behavior on which pure Ta metal was siliconized was shown in Fig. 7. This figure shows that the weight gain (mg/cm^2) of Ta sheets obeys a parabolic rate law, with a two-step siliconizing.

Next, Photo. 3 shows representative sectional features of these test pieces. The formation of alloy layers was very slow and the structure of them was not clear for a short time (4 and 9 hr), but after 16 hr the layer was thickened and a metal/alloy interface was flat and also the adhesion between metals and alloys seemed to be good. For comparison the hardness of the surface was examined and the metal subtsrate was about Hv=115, while alloy layer showed Hv=1032

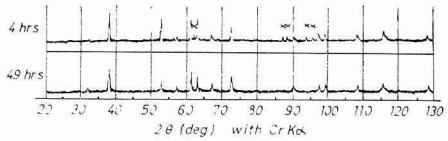
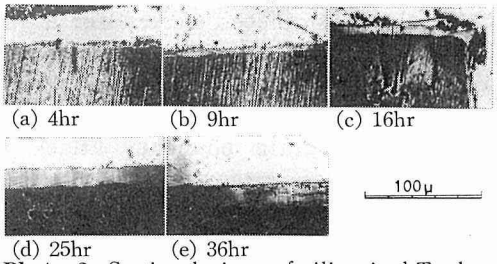


Fig. 6 X-ray diffraction patterns from siliconized Ta
(a): 4hr, ((b): 49hr. x: Ta_5Si_3, others: $TaSi_2$



(a) 4hr (b) 9hr (c) 16hr
(d) 25hr (e) 36hr

Photo. 3 Sectional views of siliconized Ta sheets at 1000°C; upper part Ni plated, lower part: Ta; intermediate layer: silicide

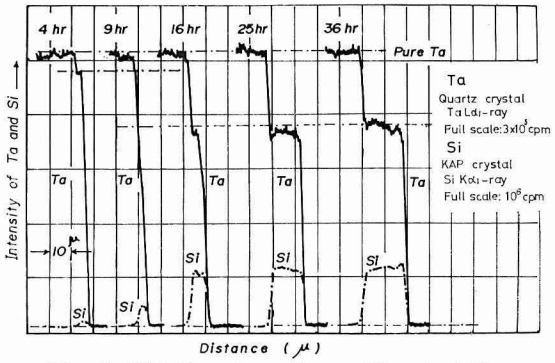


Fig. 8 EPMA patterns from siliconized Ta

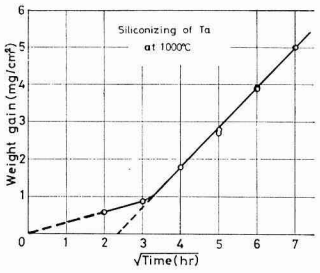


Fig. 7 Siliconizing of Ta sheet at 1000°C

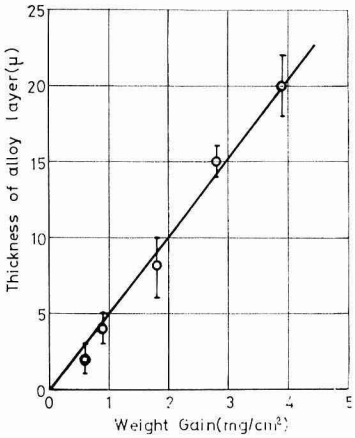


Fig. 9 Weight gain vs. thickness of alloy layer of siliconized Ta sheet

±50. From the above results the alloy layer was found to be very hard, so that this coating may be very useful for the other fields such as antiabrasive parts.

The distribution of Si as well as Ta in the treated section was examined by an EPMA method with results as shown in Fig. 8. In this figure another compound in case of the low concentration of Si for short-time treatments was present (4 and 9 hr). This wes identified as Ta_5Si_3. After a 9 hr-treatment, higher silicide was clearly seen in the figure, and the compound was determined to be $TaSi_2$ corresponding to the x-ray diffraction results. Moreover, from the detailed examination of this profile the inside of the alloy layer seemed to have a slight solubility of Si in Ta metal (in this figure it could not be indicated clearly). For example, the 16 hr-treatment showed a penetration depth of about 10 μ. Of course, the phase diagram of a Ta-Si system[10] indicates that Ta has a solubility of about 0.02 wt% of Si, so that the above stated observation is highly probable. Furthermore, the $TaSi_2$ compound has no solubility in the present phase diagram, but in a diffusion treatment such as the present investigation a calculation from the figure of the results for 36 hr-treatment showed to have a solubility range of about 1.4 wt% Si.

As the thickness of an alloy layer for different treating intervals also indicated the same relation against the square root of time as Fig. 7, the thickness of an

alloy layer was found to have a linear relation with siliconized amount (mg/cm^2) as shown in Fig. 9. But there is a certain veriety of layer depths at different positions even in the same test piece.

3.3 Oxidation of siliconized Ta sheets

In order to compare the anti-oxidation property of siliconized Ta sheets with that of pure Ta ones, Ta sheets siliconized for various intervals were oxidized for 15 min at 1000°C under the same condition as that of the latter. Fig. 10 shows the results obtained. This indicates that test pieces treated for a short time were severely oxidized, but an amount of oxidation was markedly decreased in those siliconized for 9 hr. For example, the 4 hr-treated test piece was almost covered with the white powdered oxide covering the surface, but those treated for a long time showed only a slight oxidation and a grain boundary attack was noted. These oxidized surfaces were also checked by means of an x-ray diffractometer as seen in Fig. 11, in which it was revealed that the test piece treated for 4 hr had the same patterns of simple Ta_2O_5 oxide and some of those of the original $TaSi_2$ alloy. The surface of a 49 hr-treated sheet is considered almost the same as the original one.

Here it is noteworthy that the existence of Si oxide was not recognized and it is considered that there is no Si oxide on the test piece. However, the Si oxide might be not detectable by means of an x-ray diffractometer because of its amorphous structure even if it was contained in the oxide scale. For the purpose

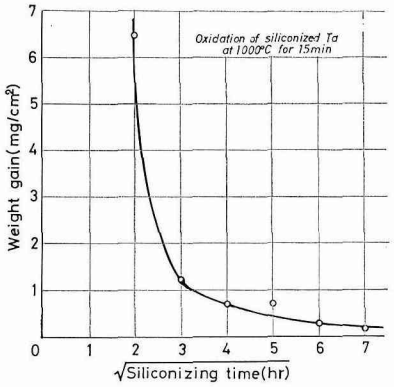


Fig. 10 Oxidation of siliconized Ta at 1000°C

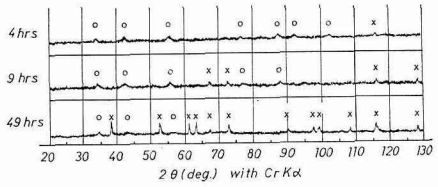


Fig. 11 X-ray diffraction patterns from oxidation of siliconized Ta
o: Oxide (Ta_2O_5), x: $TaSi_2$

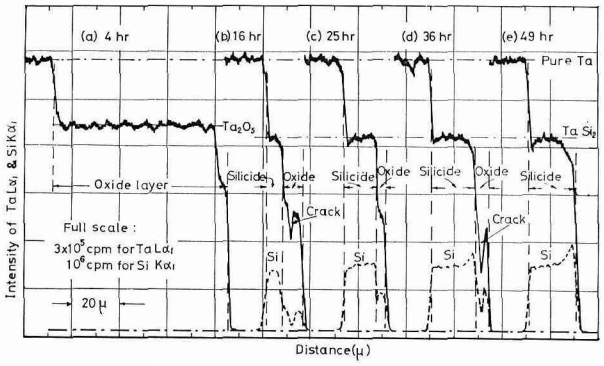


Fig. 12 EPMA patterns from oxidized Ta sheet after siliconizing for various times

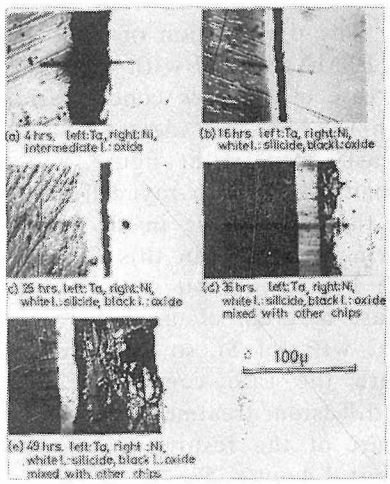


Photo. 4 Sectional views of oxidized Ta sheets after siliconizing for various times

of the detection of the existence of such an oxide, the newly prepared pure Si powder was oxidized for more than 1 hr under the same condition as before, but still such oxide could not be detected. Hence it is probable that some oxide film may exsist in spite of the lack of a reliable detection method. This shall also be discussed later in the paragraph where checking with an EPMA method will be described.

Photos. 4 (a) to (e) indicate some of the sectioned microstructures of oxidized samples. According to Photo. 4 (a) the test piece after 4 hr-treatment has the same metal/oxide interface as pure Ta sheets corresponding to the EPMA result (Fig. 12) and the alloy layer is already destroyed (refer Fig. 12 (a)). In this case it is clear that the oxide layer reaches the Ta substrate.

Moreover, there is a characteristic distribution of constituents, i. e., Si seems to enrich the oxide. Accordingly, it may be surmized that there may be some Si oxide in the scales, in spite of the fact that the compound is unknoun. Another special feature which is notable is that there is an even more enriched zone of Si in the alloy layer than the concentration before oxidation. This is probably attributable to the migration of Si toward the alloy layer during the oxidation process.

3.4 Kinetics of the oxidation of siliconized Ta sheets

In order to investigate the oxidation behavior of siliconized Ta sheets, 49 hr-treated test pieces were used at 1000°C up to 70 min. The results obtained are shown in Fig. 13. From the observation it is suggested that siliconized Ta sheets were oxidized obeying a parabolic rate law with a much lesser corrosion rate (rate constant $k=0.181$) than that of the pure Ta sheet ($k=4.0$).

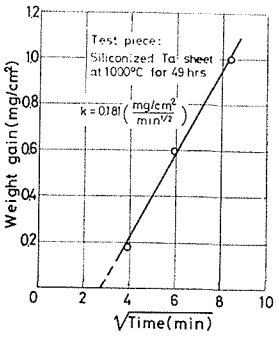


Fig. 13 Oxidation of siliconized Ta sheet at 100°C

4. Consideration of results

From the above stated results it is suggested that the oxidation behavior is closely related to the siliconizing (mg/cm^2) as seen in Fig. 14. It is quite clear shat the siliconizing amount of about 1 mg/cm^2 shows a strong suppressing effect against oxidation. Moreover, another semi-log expression of the above relation is shown in Fig. 15. There are two stages in the behavior, namely the first stage of the reaction corresponds to the oxidation in which the weight gain decreases largely with the increase in an amount of siliconizing. The latter stage of the curve involves further the oxidation of remaining Ta silicide ($TaSi_2$) in the substrate and the weight gain by oxidation decreases in proportion to an amount of siliconizing in this representation, so that these two stages must be discussed separately.

Of course, the former stage of oxidation corresponds to that of Ta-rich silicide (Ta_5Si_3) as stated before. Thus, the oxidation of this alloy layer will be relatively rapid and under the present experimental conditions the alloy layer is oxidized up to the thickness formed after 9 hr-treatment. Nevertheless, the thin oxide layer formed strongly retarded further oxidation.

Here, considering the latter stage of the oxidation, it would be, at first, necessary to clarify the relation between the oxidation of this alloy layer and the

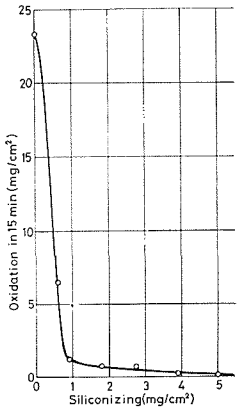


Fig. 14 Siliconizing vs. oxidation

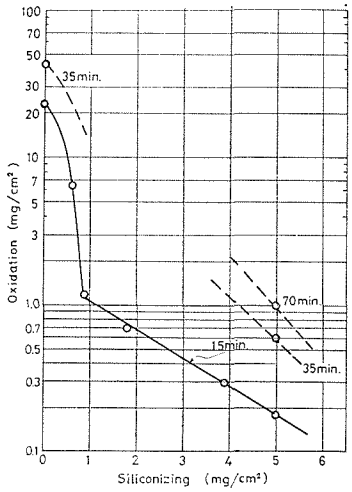


Fig. 15 Oxidation vs siliconizingcurve for Ta sheet at 1000°C

diffusion behavior of Si atoms in this layer. The observation that in the latter stage the oxidation is not too extensively retarded even with a relatively thick alloy layer will be explained by another mechanism. It is generally assumed that Si atoms migrate into Ta metal and then the released Ta atoms at the interface will combine with oxygen atoms because oxygen atoms readily migrate through the oxide. If Si atoms only migrate towards Ta in the alloy layer and Ta atoms only combine with oxygen, then Si atoms will be forced to migrate into the Ta metal leaving only Ta oxide behind, so that the $TaSi_2$ layer will not change its thickness even after oxidation for a long time.

we then examined whether the above stated assumption of the oxidation of alloy layers was valid by using 49 hr-treated test pieces. However, the change in the thickness of alloy layer could not be clearly recognized before and after the oxidation for about 1 hr because of the small variation of each alloy layer formed under the same conditions and the irregularity of the alloy thickness at various positions of the same test piece. Accordingly, it is suggested that the flux of Si atoms will decrease with the thicker alloy layer on account of the decrease in the concentration gradient, so that Ta atoms remaining on the surfaces per unit time will be increasingly decreased by thicker layers, resulting in the decrease of the oxidation of the alloy.

Since it is recognized from the EPMA penetration curve in the sectioned alloy layer that there are some amount of Si even in the oxide layer and that Si is much enriched in the alloy near the alloy/oxide interface, the above assumption will be partly valid.

5. Conclusion

Ta sheets were siliconized in the pure Si vapor in an evacuated quartz ampoule up to 49 hr at 1000°C, and then oxidized in flowing air in order to compare with the results of oxidation of pure Ta sheets for 15 min at 1000°C. The results obtained were as follows:

(1) Siliconizing of Ta sheets obeys a parabolic rate law and shows a two-stage behavior, the first is formation of a lower silicide layer (Ta_5Si_3) with a slower

rate, and next after about 9 hr the second stage corresponding to the formation of a higher silicide layer ($TaSi_2$) with a higher growth rate occurs.

(2) Oxidation of pure Ta sheets showed an anomalous behavior in which the corners of a test piece were strongly oxidized and curled back in spite of the fact that the center of the sheets were of a compact type. However,both oxides show the same compound (Ta_2O_5) with different growth orientations at each positions. By using alumina markers this chemical process was determined to proceed with the inward diffusion of oxygen atoms through Ta oxide.

(3) Oxidation of siliconized Ta sheet showed a greater resistance with the increase in the amount of siliconizing and the behavior of oxidation was divided into two stages corresponding to the formation of two kinds of silicides. The former stage showed a large decrease of corrosion because of the protection of oxide against further oxidation and the latter one did not show too large a resistance and could be controlled with the inward diffusion of Si atoms through the silicide layer after the formation of an initial oxide layer. In the present experiment the oxidation of Ta sheets showed a retardaition down to about one hundredth on account of the siliconized layer formed in 49 hr at 1000°C.

Acknowledgement

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