Characterization of Graded Ti Silicide Coating Formed by Thermal Diffusion Treatment of Low Pressure Plasma Sprayed Silicon Coating on Titanium Substrate †

Akira OHMORI*, Kohei YOSHIDA** and Chang-Jiu LI***

Abstract

The silicon coating was sprayed on a titanium substrate by low pressure plasma spraying and the resulting coating was heat-treated in vacuum. It was found that a titanium silicide coating with the composition changed gradually can be formed through thermal diffusion treatment of silicon coating formed in this way. The silicide coatings were characterized by optical microscopy, scanning electron microscopy, EPMA analysis and X-ray diffraction (XRD). The forming process of the silicide coating were investigated by examining the relationship between silicide coating thickness and thermal diffusion parameters. The results show that the composition of the silicide coating changes gradually from $TiSi_2$ at the silicon coating side through TiSi and Ti_5Si_4 to Ti_5Si_3 near the substrate side. The thickness of such graded silicide coating is determined by temperature and holding time during heat-treatment. The diffusion of silicon into titanium substrate is mainly responsible for the formation of silicide. Moreover, the investigation of the oxidation behavior of the silicide coating shows that the formation of silicide coating on the titanium substrate can improve the oxidation resistance of titanium.

KEY WORDS:(Graded Ti silicide coating) (Oxidation) (Thermal diffusion) (Low pressure plasma spray) (Silicon coating) (Ti substrate)

1. Introduction

Titanium silicide, like other refractory metal silicides, is generally of special interest in semiconductor processing due to its excellent chemical and thermal stability and low electric resistivity [1]. Because of its lowest resistivity among the refractory metal silicides, titanium silicide has been primarily intensively studied for electronic materials[2-6].

Recently, molybdenum disilicide ($MoSi_2$) has attracted considerable attentions as an elevated-temperature structure material, as a result of its combination of physical properties especially high temperature oxidation resistance and high modulus at elevated temperature [7]. With regarding to titanium silicide, there are few studies which consider it as an engineering structural material.

On the other hand, with the application of titanium alloys in high temperature environments, it is expected that the protection of titanium from oxidation would become necessary.

The formation of titanium silicide is usually carried out by a metallurgical diffusion process through the annealing of thin titanium film deposited on silicon [2,5]. Several kinds of silicides such as Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$ can be formed depending on the processing conditions [3]. Therefore, titanium silicide is generally used in the form of thin film. When such film is formed on a titanium alloy surface, it can expected to be used as a potential protective coating.

In the present paper, the characteristics of the formation of titanium silicide are investigated by depositing silicon by low pressure plasma spraying on a titanium substrate and subsequent annealing treatments aimed at the effective protection of titanium alloy from oxidation under elevated temperature.

2. Materials and Experimental Procedure

Feedstock used was commercially available pure silicon powder (Powderex R-92-67), the grain size of which ranged from 10 to 75mm. An industrial pure titanium plate of 3 mm in thickness was used as a substrate, and was sand-blasted before spraying.

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* Professor
** Graduate student of Osaka Univ.
*** Professor, Xi'an Jiao Tong Univ.

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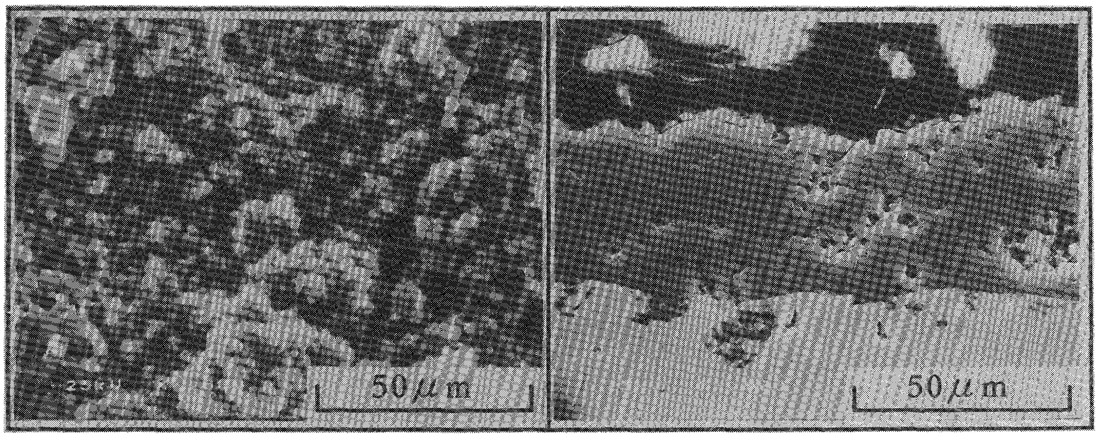


Fig. 1 SEM microstructure and surface morphology of as- sprayed Si coating

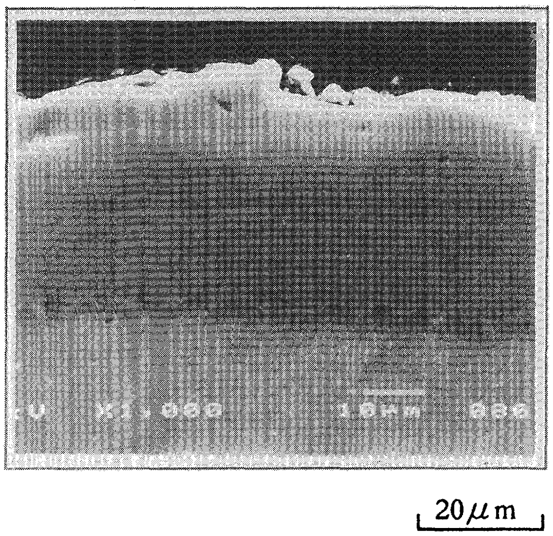


Fig. 2 Typical Ti silicide graded layer formed at 1523 K for 10.8ks

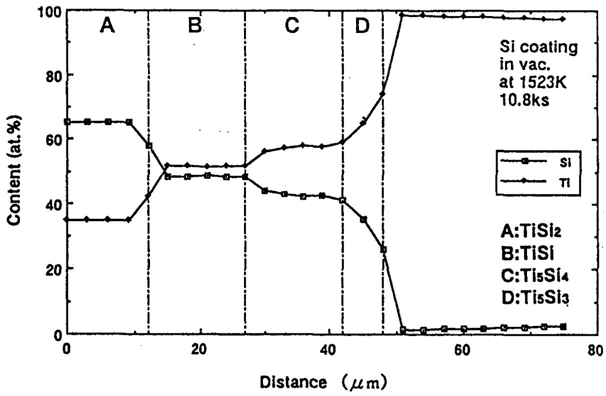


Fig. 3 Typical EPMA analysis result of Ti silicide graded coating formed at 1523K for 10.8ks

The plasma spraying of silicon was carried out in an argon atmosphere. The pressure of spray chamber was $2.7x10^4$Pa. Before the arc was ignited the chamber was evacuated to a pressure lower than $1.3x10^2$Pa. Then, the chamber pressure was adjusted to $2.7x10^4$Pa by charging with argon gas before the arc ignition. The plasma torch used was a Metco 7MB type. The primary operating gas of the arc was argon, operated at the pressure 0.7MPa and flow rate of 47l/min. Secondary gas was hydrogen, operated at 0.7MPa. The power of the plasma arc was 36kW. Spray distance was kept at 250mm.

The sprayed samples were annealed in a vacuum furnace. After the furnace was evacuated to a pressure of $1.6x10^{-3}$ Pa, the temperature of samples was raised at a heating rate of 0.14K/s till a certain temperature was reached. Then the isothermal annealing was carried out for pre-determined holding times.

The oxidation of annealed samples was carried out in a furnace at ambient atmosphere at different temperatures for different holding times.

The microstructure of annealed samples was characterized by X-ray diffraction (XRD), EPMA.

3. Experimental results and discussion

3.1 The microstructure of annealed silicon coating sprayed on titanium substrate

Figure 1 illustrates the surface morphology and cross sectional structure of an as-sprayed silicon coating. XRD analysis showed that the as-sprayed coating consisted of silicon phase only.

Figure 2 shows a typical microstructure of a sample annealed at 1523K for 10.8ks. It can be clearly recognized that the annealed coating consists of different layers. From the EPMA analysis result of the annealed sample shown in **Fig.3**, it can be recognized that there exists a diffusion zone from the titanium substrate side towards the coating surface with the compositions of titanium and silicon changing gradually. Evidently, there exist three distinct layers which are marked as A, B and C in Fig.3. From the XRD pattern of the annealed coating illustrated in **Fig.4,** it can be found that four kinds of silicide phases were recognized. Those phases are Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$. Compared with EPMA analysis results those phases correspond to the diffusion zones of A, B, C and D shown in Fig.3, although the region with the phase of Ti_5Si_3 was not remarkable. Therefore, from the silicon coating surface side to the substrate the silicates formed are $TiSi_2$, TiSi, Ti_5Si_4 and Ti_5Si_3, the compositions of which are gradually changing.

3.2 The forming process of titanium silicide coating

The annealing experimental results clearly show that the silicides can be formed at the interface between the sprayed silicon coating and the titanium substrate through annealing. Evidently, the formation of such graded silicide coating proceeds through thermal diffusion process.

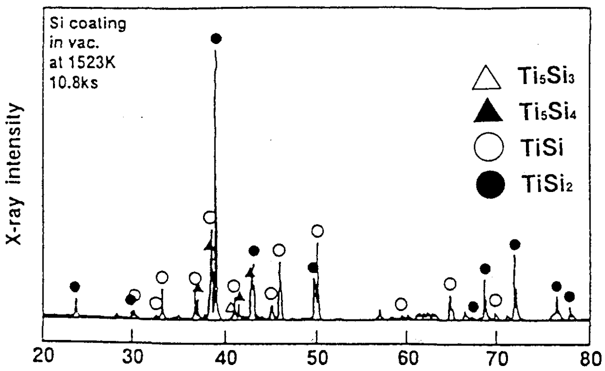


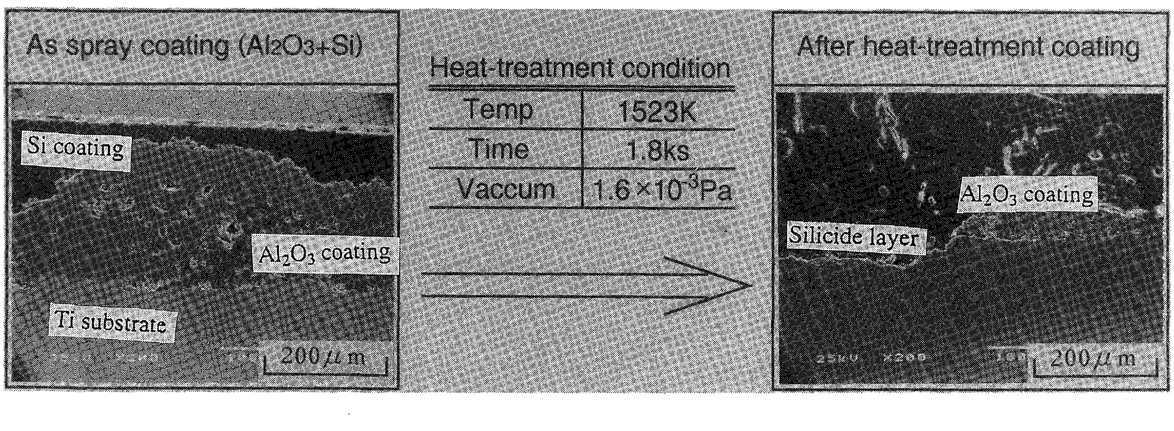
Fig. 4 Typical ERD pattern of Ti silicide graded coating formed at 1523K for 10.8ks.

In order to confirm the dominant diffusion element, alumina coating was sprayed partially on titanium substrate as the marker before the spraying of silicon coating. **Figure 5** (a) and (b) illustrate the as-sprayed sample and the sample annealed at 1523 K for 1.8 ks. From Fig.5 (b), it can be seen that the interface between silicide and titanium substrate moved about 50μm towards the substrate side compared with the interface between alumina coating and titanium substrate. This fact suggests that the diffusion of silicon towards the titanium substrate is mainly responsible for the formation of silicides.

3.3 Growth characteristic of titanium silicide coating

Figure 6 and Fig. 7 show the microstructures of cross sections of annealed silicon coating on titanium substrate under the temperature of 1473K and 1573K for holding times from 1.8ks to 21.6ks. It can be recognized that the silicide coatings were formed in all cases and the thickness of silicide coatings is increased with an increase in holding time. During the experiments, it was found that the surface layer including silicon tended to chip off from the inside of the $TiSi_2$ layer after the sample cooled to room temperature owing to the cracking of the surface layer, especially at high temperature of 1573K. Therefore, it was difficult to obtain a graded titanium silicide with all $TiSi_2$ retained in the coating under high temperature.

By EPMA analysis, the relationship between the thickness of titanium silicide and holding time was examined. It was found that for the silicide includingTi$_5$Si$_3$, Ti_4Si_3 and TiSi, the total thickness grows



(a) (b)

Fig. 5 The microstructure of as-sprayed silicon coating on Ti substrate with Al_2O_3 interlayer (a) and subsequently annealed at 1523K for 1.8ks(b).

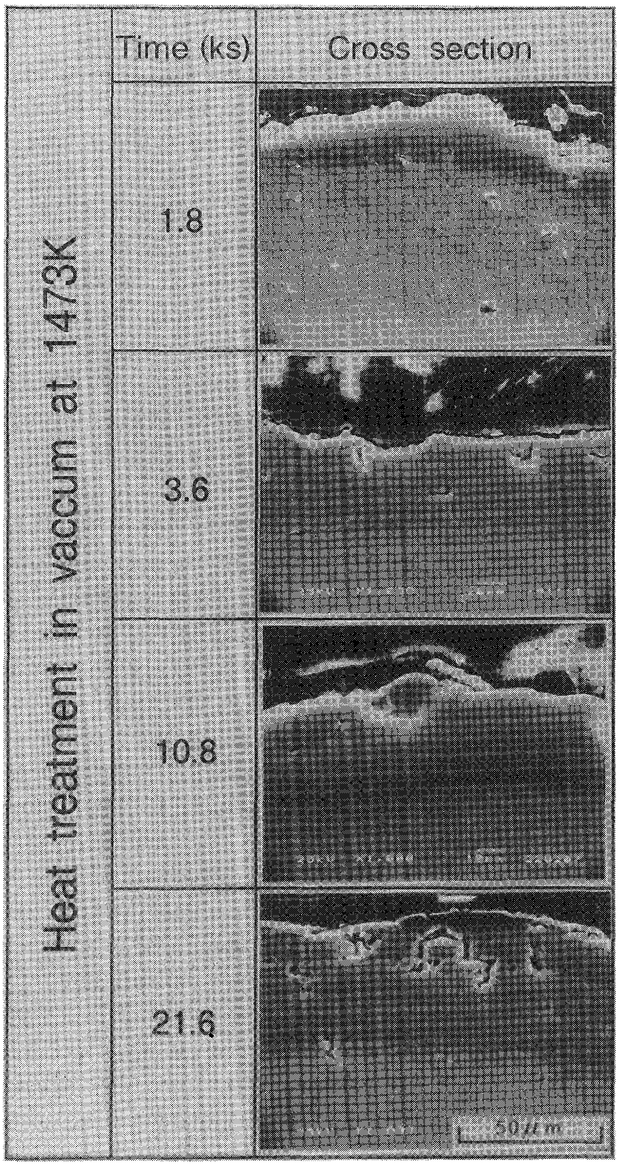


Fig. 6 Microstructure of silicon coating annealed at 1473K for different holding times

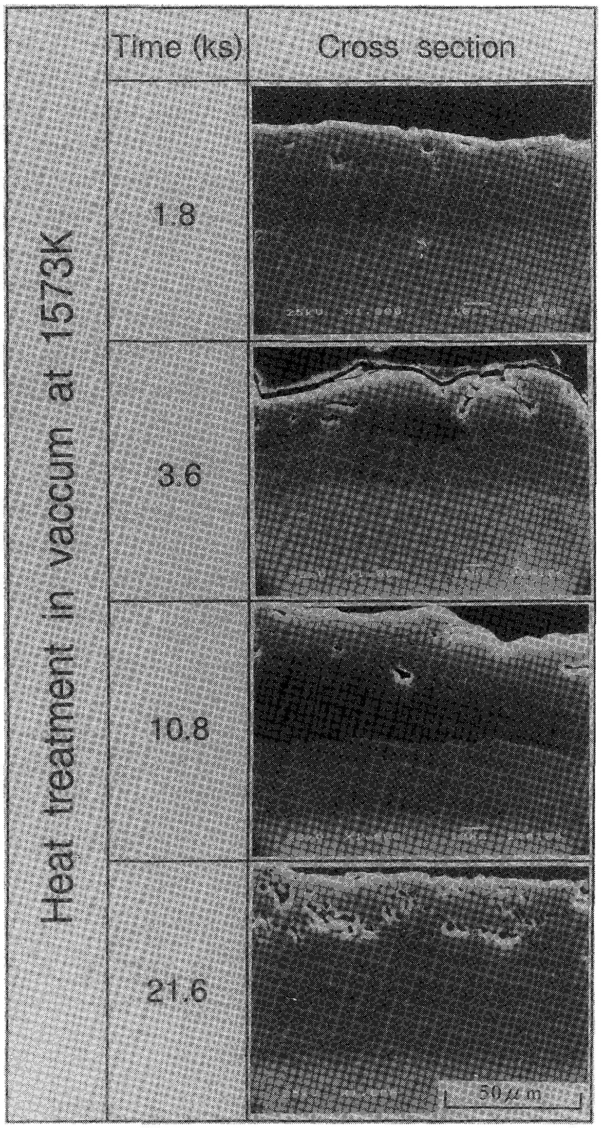


Fig. 7 Microstructure of silicon coating annealed at 1573K for different holding times.

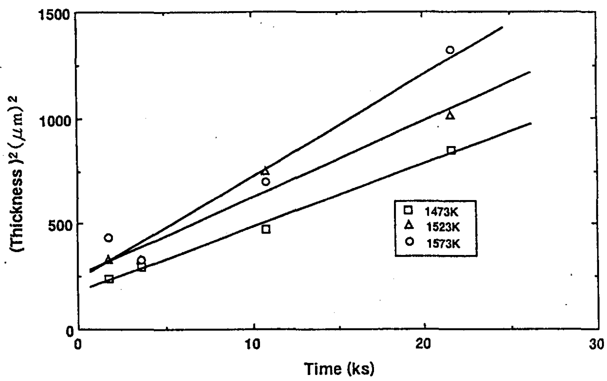


Fig. 8 The relation between Ti silicide graded coating layers (TiSi + Ti_5Si_4 + Ti_5Si_3) thickness and holding time at different annealing temperatures.

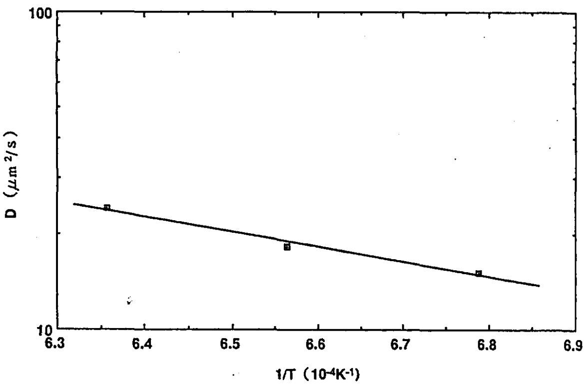


Fig. 9 Arrhenius plot for the growth rates of Ti silicide graded layers. (TiSi + Ti_5Si_4 + Ti_5Si_3)

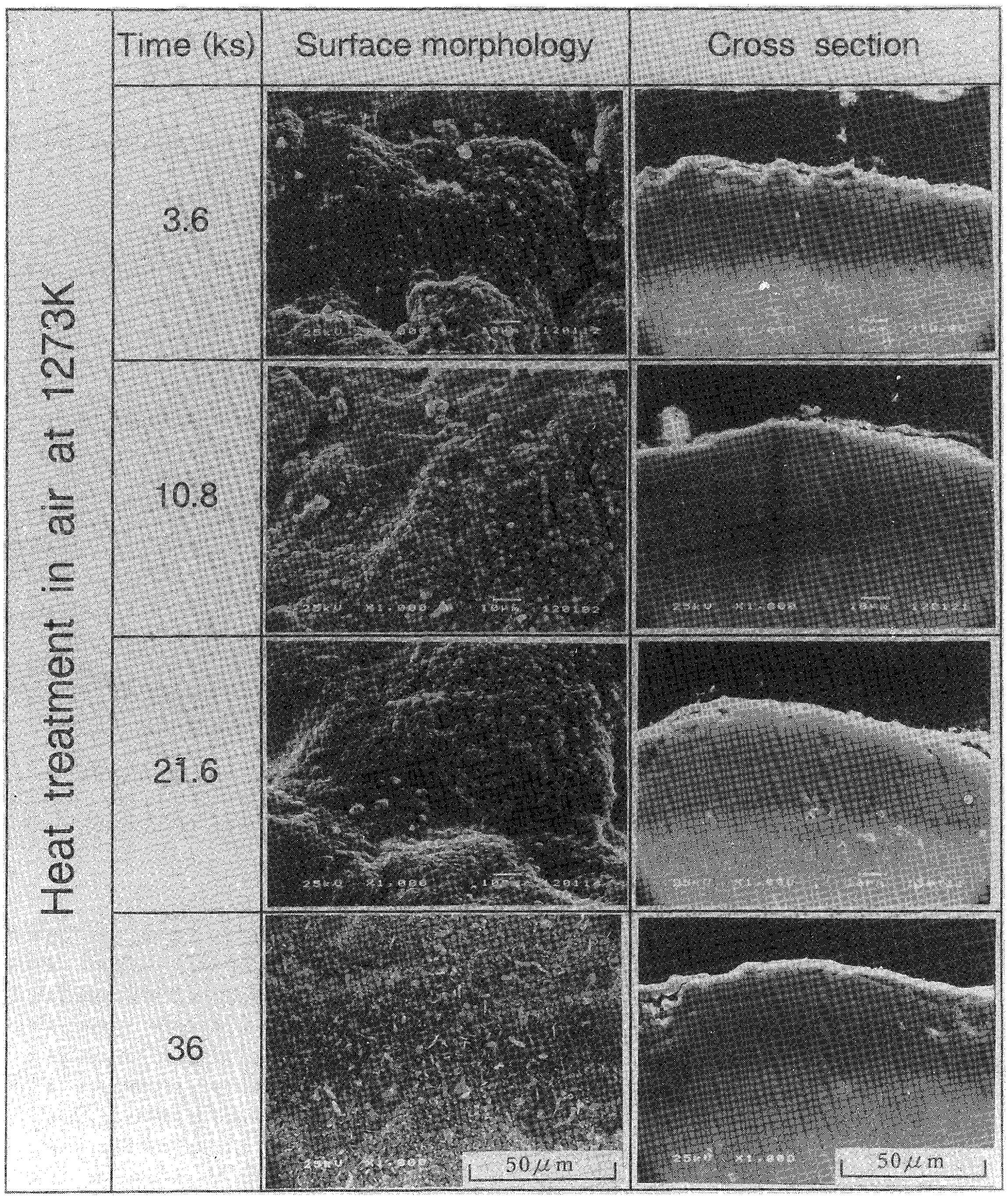


Fig. 10 Microstructure and surface morophology of Ti silicide graded layers on Ti plate after oxidation at 1273K for different times

parabolically with time, as shown in **Fig.8**. **Figure 9** show the Arrhenius plot for the growth rates of Ti silicide graded layers. The estimation of apparent activation energy from the Arrhenius relation for the titanium silicide forming process yielded a value of 0.92 eV/atom.

For titanium silicide, the investigation of growth kinetics has been mainly carried out for $TiSi_2$, which yielded the activation energy of 1.8eV. Present results yielded a lower value for TiSi, Ti_5Si_4 and Ti_5Si_3 (except $TiSi_2$), compared with that of $TiSi_2$. This fact may suggest that the formation of those phases is relatively easier than that of $TiSi_2$.

3.4 Oxidation behavior of graded titanium silicide coating

The sample with titanium silicide coating used for oxidization experiment was prepared by annealed silicon sprayed on titanium under vacuum at temperatures of 1473K for 10.8ks. All samples were confirmed to have a complete graded titanium silicide coating from Ti_5Si_3, Ti_4Si_3, TiSi to $TiSi_2$ by XRD before they were oxidized at ambient atmosphere.

Figure 10 shows the microstructure and surface morphology of the sample oxidized at 1273K for different times. It can be found that after 21.6ks oxidizing, the graded titanium silicide coating still consists of three identical layers. XRD analysis from the surface of oxidized sample revealed that the titanium silicide $TiSi_2$ near the coating surface was mainly oxidized to TiO_2 at the temperatures of 1273K and 1373K. At the temperature of 1473K, a small amount of SiO_2 was recognized in the surface layer besides TiO_2 resulted from the oxidization of $TiSi_2$ near the heated coating surface. XRD analysis also showed that with the increase in holding time for oxidization the ratio of main peaks of TiO_2 to $TiSi_2$ in the XRD patterns of oxidized samples increased. Moreover, the EPMA analysis showed that although the $TiSi_2$ layer thickness under the silicon coating decreased with the increase in holding time, the other titanium silicides under $TiSi_2$ were not changed significantly as shown by **Fig.11**. After oxidation for about 21.6ks at 1273K, most of the $TiSi_2$ layer formed was consumed. For comparison, **Fig.12** shows the microstructure of cross sections of bare titanium plate oxidized under the temperatures of 1273K, 1373K and 1473K for 3.6ks. It can be seen that at 1273K for 3.6ks the oxidized layer reached over 50μm. Therefore, from these results, it is clear that the oxidization resistance of titanium can be significantly improved by forming a graded titanium silicide coating at the surface, although it should be indicated that at 50μm, oxidation resistance Ti silicide coating should be improved.

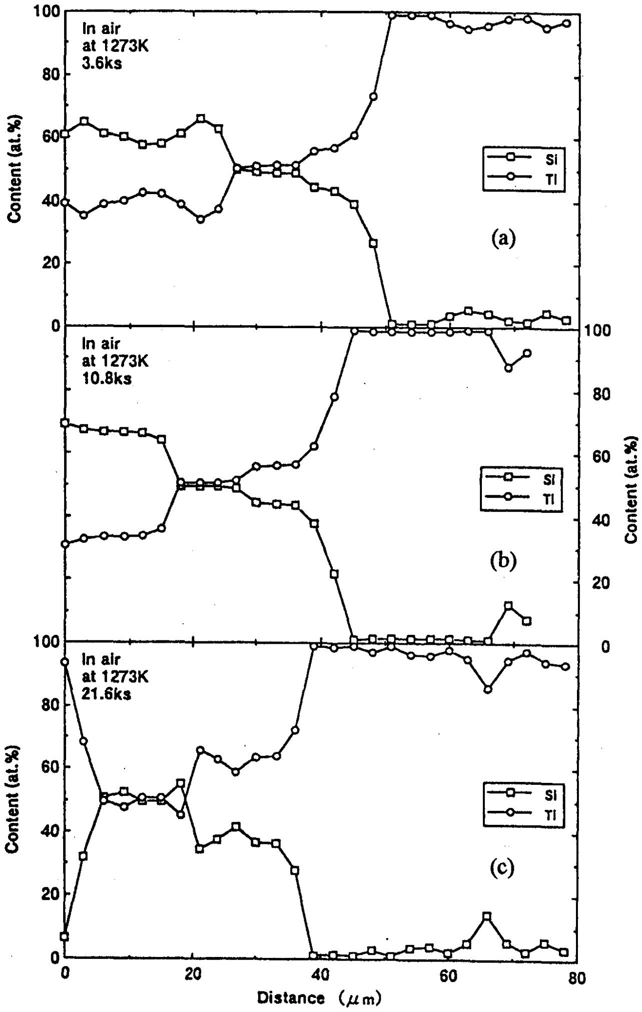


Fig. 11 The EPMA analysis results of the compositions of graded Ti silicide coating after oxidation at 1273K for different times: (a) 3.6ks, (b) 10.8ks, (c) 21.6ks

4. Conclusions

The Titanium silicide coating was formed through a silicon coating sprayed on a titanium substrate by low pressure plasma spraying and subsequent heat-treatment in vacuum. It was found that a titanium silicide coating with the composition changing gradually can be formed through thermal diffusion treatment of silicon coating sprayed by low pressure plasma on titanium substrate. The composition of silicide coating changes gradually from $TiSi_2$ at the silicon coating side through TiSi and Ti_5Si_4 to Ti_5Si_3 near the substrate side. The thickness of such a graded silicide coating is determined by temperature and holding time during heat-treatment. The diffusion of silicon into the titanium substrate is mainly responsible for the formation of silicide. Moreover, the formation of silicide coatings on the titanium substrate can improve the oxidation resistance of the titanium.

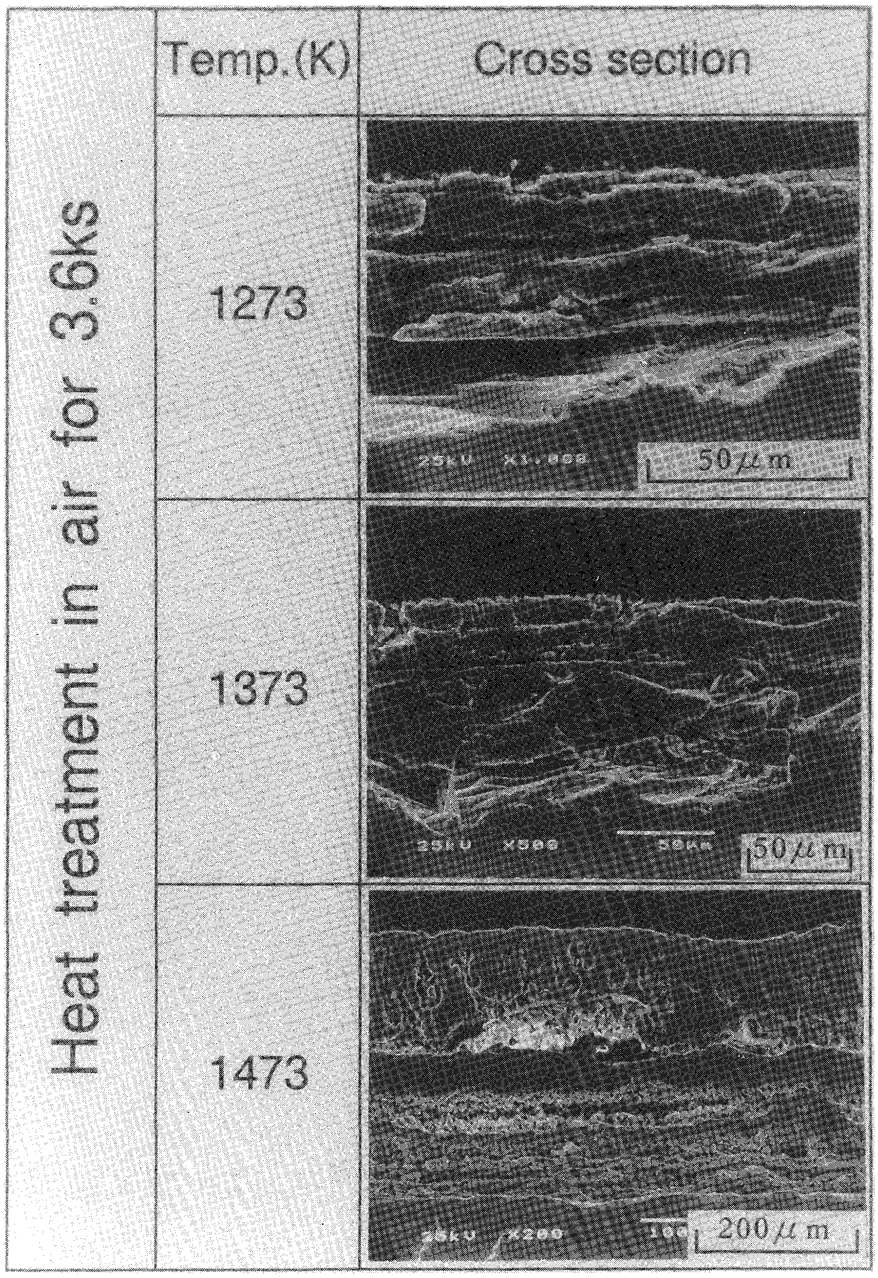


Fig. 12 Cross-section of pure Ti plate after oxidation at different temperatures for 3.6ks.

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