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# Classification of Oxidation Behavior of Disilicides

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**Abstract.** This study focuses on classification of structures of oxide scales formed on disilicides. The oxide scales formed on disilicides can be grouped into 3 types, (a) silica scale, (b) mixed oxide (silica+metal oxide) scale, and (c) double layered (silica/metal oxide) scale. Disilicide that forms an oxide scale of the type (a) generally show excellent oxidation resistance. As such disilicides, there are  $\text{FeSi}_2$ ,  $\text{CoSi}_2$ ,  $\text{MoSi}_2$ ,  $\text{WSi}_2$ , etc. In  $\text{FeSi}_2$  and  $\text{CoSi}_2$ , a protective silica scale must be formed due to the selective oxidation of Si, whereas in  $\text{MoSi}_2$  and  $\text{WSi}_2$  evaporation of metal oxide plays an important role for the formation of a silica scale. Oxidation of  $\text{TaSi}_2$  and  $\text{NbSi}_2$  belonged to the type (b), and only  $\text{CrSi}_2$  the type (c).

## Introduction

Disilicides such as  $\text{MoSi}_2$  are receiving much attention as high-temperature materials because of the extremely-high oxidation resistance based on formation of a protective silica scale. However, oxidation mechanism of disilicides has not been clarified yet. In other words, thermodynamic and kinetic conditions for formation of a protective silica scale are not well-known.

In the field of advanced jet engines and gas turbines, development of ultra-high temperature structural materials is indispensable. Disilicides are expected to be promising candidate materials because of high melting point and relatively low density. Moreover, Some refractory metal disilicides, for example  $\text{MoSi}_2$  [1-3] and  $\text{WSi}_2$  [4,5], show excellent oxidation resistance at high temperatures. This is due to the formation of a protective  $\text{SiO}_2$  scale by selective oxidation of Si. However, oxidation behavior of disilicides is generally complicated, especially depending on oxidation temperature. Therefore, oxidation mechanism for each disilicide has not been clarified yet.

In the present study, based on observation of structures of oxide scales formed on some disilicides, classification of oxidation behavior in disilicides was proposed and oxidation processes were discussed.

## Experimental

**Fabrication of specimen:** Powders of disilicides such as  $\text{FeSi}_2$ ,  $\text{CoSi}_2$ ,  $\text{MoSi}_2$ ,  $\text{WSi}_2$ ,  $\text{CrSi}_2$ ,  $\text{NbSi}_2$ ,  $\text{TaSi}_2$ ,  $\text{VSi}_2$ , and  $\text{ReSi}_{1.75}$ , were sintered by applying a spark plasma sintering (SPS) method. In this sintering method, the each powder is packed in a graphite die (outer diameter: 25 mm and inner diameter: 15 mm) under a compressive stress of 40 MPa, and then a pulsating current was passed through the powder and the graphite die in an evacuated chamber of 6 Pa. The heating rate was 0.33 K/sec, and pulsating current was passed to heat up to each sintering temperature in which full densification of the disilicide can be achieved. Relative densities measured by Archimedeian method were over 96% in all disilicides.

**Oxidation tests:** Specimens for oxidation tests were cut into about 4x7x1 mm pieces from the sintered compacts. The surfaces were polished to 1  $\mu\text{m}$  diamond finish, and then cleaned ultrasonically in acetone bath. Although oxidation tests were carried out in air at temperatures

ranging from 773 to 1773 K, the oxidation temperature range depends on the melting point and phase transformation temperature of each disilicide. Observation and analysis of oxide scales formed on the disilicides were performed with scanning electron microscopy (SEM), transmission electron microscopy(TEM), and electron probe microanalyzer (EPMA).

## Results and Discussion

**Prediction of oxidation mode:** In oxidation of disilicides, selective oxidation of Si or simultaneous oxidation of metal and Si could be observed. Thus, the oxidation reactions are expressed as follows:



Which reaction is liable to occur would depend on thermodynamic (affinity of metal and silicon for oxygen) and kinetic (diffusivity of oxygen in oxide scale and silicon in disilicide) factors. Therefore, those factors must be considered for understanding oxidation mechanism of disilicides. Moreover, in the case that the metal oxide possesses a high vapor pressure, the evaporation must be considered. These factors in an oxidation process are illustrated in Fig. 1.

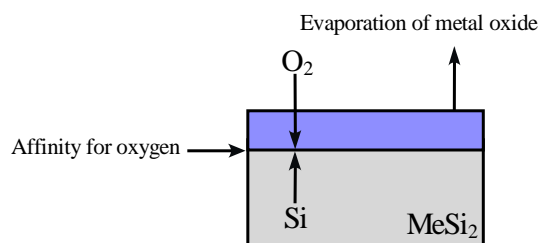


Fig.1 Thermodynamic and kinetic factors in oxidation of disilicide.

Fig. 2 shows a predicted oxidation model of disilicides. As a first step in predicting oxidation mode, we at first consider difference in affinity for oxygen between metal and Si. For the consideration, the following three cases are predicted.

- (a) Affinity of Si for oxygen is much higher than that of metal:  $\text{FeSi}_2$ ,  $\text{CoSi}_2$ ,  $\text{MoSi}_2$ ,  $\text{WSi}_2$ ,  $\text{ReSi}_{1.75}$ . In these disilicides, it is speculated that Si tends to be selectively oxidized, leading to formation of a  $\text{SiO}_2$  scale.
- (b) Affinity of Si for oxygen is relatively close to that of metal:  $\text{NbSi}_2$ ,  $\text{TaSi}_2$ ,  $\text{CrSi}_2$ . In these disilicides, it is speculated that selective oxidation of Si is hard to occur.
- (c) Affinity of Si for oxygen is lower than that of metal:  $\text{VSi}_2$ ,  $\text{TiSi}_2$ ,  $\text{ZrSi}_2$ . In these disilicides, it is speculated that metal and Si tend to be simultaneously oxidized, leading to formation of a mixed oxide scale.

As the next step, diffusivity of Si in a disilicide and oxygen in an oxide scale must be considered. Even in the disilicides belonging to (a), sufficient supply of Si from a disilicide substrate, comparing with that of oxygen through a  $\text{SiO}_2$  scale, is required for continuous growth of a  $\text{SiO}_2$  scale. In other words, in disilicides which have high diffusivity of Si in the disilicides and low affinity of metal for oxygen, steady growth of a  $\text{SiO}_2$  scale is liable to occur.

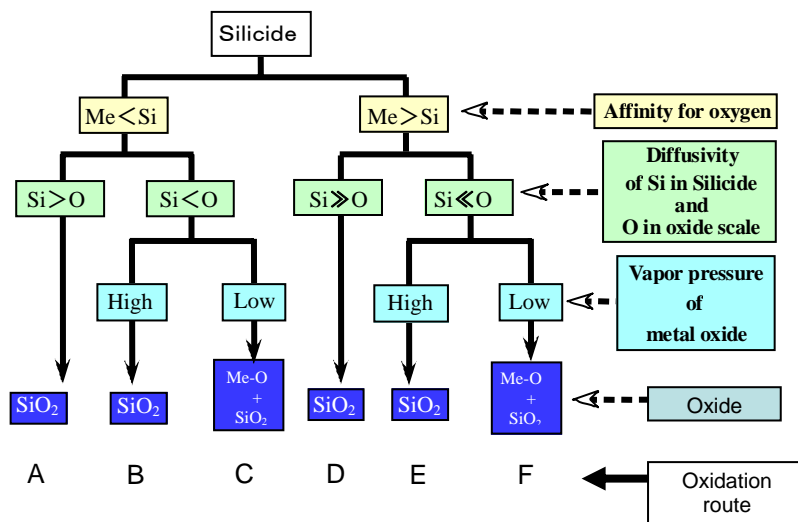


Fig. 2 Prediction of oxidation route in disilicides.

Conversely, in disilicides which have low diffusivity of Si in the disilicides and high affinity of metal for oxygen, simultaneous formation of metal oxide and SiO<sub>2</sub> is liable to occur.

In addition, when the metal oxide(s) formed on a disilicide possesses a high vapor pressure, it is speculated that evaporation of the metal oxide plays an important role in the formation of a SiO<sub>2</sub> scale. That is to say, only SiO<sub>2</sub>, as a consequence of simultaneous formation of metal and silicon oxides and evaporation of the metal oxide in an early stage of oxidation, may remain on the disilicide. The vapor pressures of MoO<sub>3</sub>, WO<sub>3</sub>, and Re<sub>2</sub>O<sub>7</sub> are appreciably high, and the high vapor pressure is particularly advantageous for forming a SiO<sub>2</sub> scale.

Depending on the above factors, the oxidation process of each disilicide will take an oxidation route among A-F shown in Fig. 2.

**Structure of oxide scale formed on disilicide:** As qualitatively described above, structure of an oxide scale formed on a disilicide could be mainly decided by thermodynamic and kinetic factors and vapor pressure of metal oxide. However, data on those factors, especially data on diffusivity, are not necessarily sufficient. Therefore, in the present study, structures of oxide scales formed on various disilicides in a wide temperature range were observed.

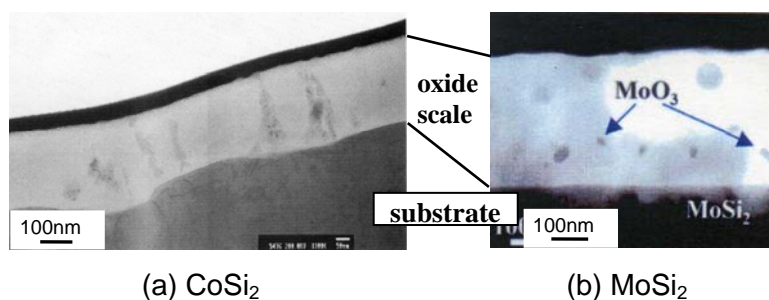


Fig. 3 TEM photographs of oxide scales formed on (a) CoSi<sub>2</sub> for 360ks at 1373 K and (b) MoSi<sub>2</sub> for 360ks at 1273 K.

(1) Disilicide in which affinity of Si for oxygen is much higher than that of metal

In oxidation of the disilicides belonging to this category, taking a route A or B can be expected. As an example, Fig. 3 shows cross-sectional TEM images of the oxide scales formed on CoSi<sub>2</sub> at 1373 K and MoSi<sub>2</sub> at 1273 K in air. It can be understood that each disilicide forms a SiO<sub>2</sub> scale almost completely at the oxidation temperature.

Structures of all oxide scales formed on CoSi<sub>2</sub> in a temperature range of 773 K to 1373 K were similar to that in Fig. 3(a). FeSi<sub>2</sub> also forms a complete SiO<sub>2</sub> scale in a temperature range of 773 K to 1273 K. Here, as maximum oxidation temperature for CoSi<sub>2</sub> and FeSi<sub>2</sub> was decided by considering melting point and phase transformation temperature, structures of oxide scales formed at higher temperatures were not observed. TEM observation of oxide scales in CoSi<sub>2</sub> and FeSi<sub>2</sub> demonstrates that Si is selectively oxidized to form a SiO<sub>2</sub> scale. This may be caused by high diffusivity of Si in the disilicides and lower affinity of Co or Fe for oxygen comparing with Si. Consequently, it can be concluded that the oxidation process of CoSi<sub>2</sub> and FeSi<sub>2</sub> takes a route A.

On the other hand, MoSi<sub>2</sub> and WSi<sub>2</sub> form a complete SiO<sub>2</sub> layer at temperatures higher than 1273 K and 1573 K, respectively, but these disilicides form a mixed oxide scale consisting of SiO<sub>2</sub> and metal oxide (MoO<sub>3</sub> or WO<sub>3</sub>) at lower temperatures. An example of the oxide scale structure is demonstrated in Fig. 4 which shows the oxide scale formed on MoSi<sub>2</sub> at 773 K. The oxide scale consists of an amorphous

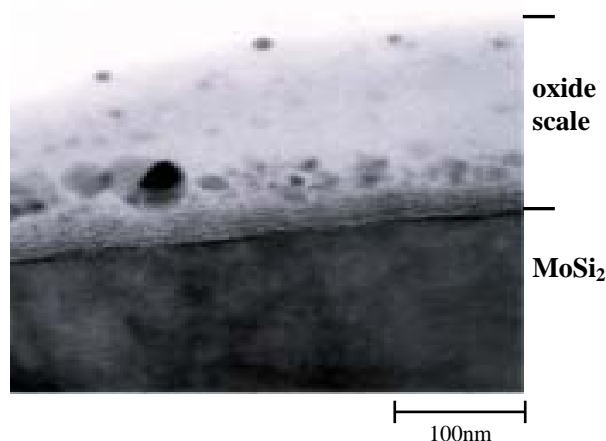


Fig. 4 TEM photograph of oxide scale formed on MoSi<sub>2</sub> for 360 ks at 773 K.

SiO<sub>2</sub> scale containing a number of fine MoO<sub>3</sub> particles. Similarly, WSi<sub>2</sub> also forms an mixed oxide scale consisting of SiO<sub>2</sub> and WO<sub>3</sub> in a low temperature region, as shown in Fig. 5. It can be seen in Fig. 5 that the oxide scales formed on WSi<sub>2</sub> are grouped into 3 types, depending on oxidation temperature. At temperatures below 1073 K, the oxide scales consist of the mixed oxides of WO<sub>3</sub> and SiO<sub>2</sub>. In the intermediate temperature range, oxide scales having double-layer structure are formed. The outer and inner layers are consisting of SiO<sub>2</sub> and the mixed oxides of WO<sub>3</sub> and SiO<sub>2</sub>, respectively. At temperatures above 1573 K, an oxide scale consisting of only SiO<sub>2</sub> is formed. The formation of the outer SiO<sub>2</sub> layer in the intermediate temperature range must be caused by evaporation of WO<sub>3</sub>. In other words, evaporation of WO<sub>3</sub> plays an important role for the formation of a complete SiO<sub>2</sub> layer.

At the moment when WSi<sub>2</sub> is exposed to an oxidizing atmosphere, W and Si must be simultaneously oxidized to form WO<sub>3</sub> and SiO<sub>2</sub>. In the case that the vapor pressure of WO<sub>3</sub> is appreciably high, it is expected that only SiO<sub>2</sub> is liable to be left on the substrate. In fact, the oxide scales formed at temperatures above 1573 K consisted of only SiO<sub>2</sub>. Once the substrate is covered with a protective SiO<sub>2</sub> scale, only SiO<sub>2</sub> grows in further oxidation. In other words, selective oxidation occurs. However, at lower temperatures, the evaporation rate was not enough to left only SiO<sub>2</sub>. Therefore, WSi<sub>2</sub> forms a mixed oxide scale at low temperatures and a double layer oxide scale at intermediate temperatures.

Based on such structure of oxide scales formed in the intermediate temperature region, the requisite vapor pressure of metal oxide for formation of a complete SiO<sub>2</sub> scale can be estimated. Our recent study on some disilicides demonstrated a clear relationship between vapor pressure

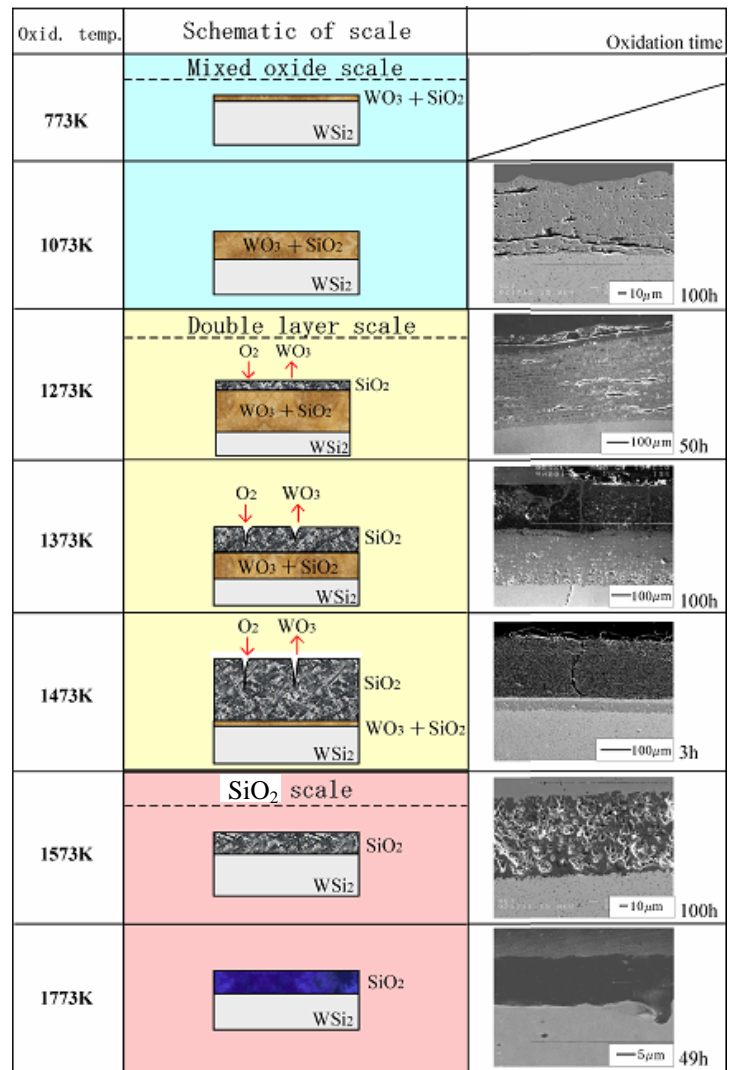


Fig. 5 Cross-sectional SEM photographs of oxide scales formed on WSi<sub>2</sub> at various temperatures.

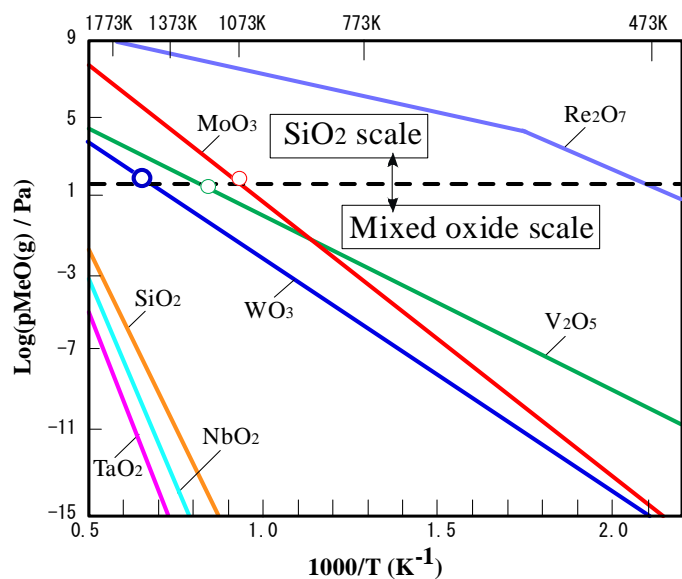


Fig. 6 Vapor pressure of various metal oxides.

of a metal oxide and formation of a SiO<sub>2</sub> scale [6]. The relationship is shown in Fig. 6, where open circles indicate the approximate transition temperatures from the formation of a double layer scale to that of a SiO<sub>2</sub> scale. In MoSi<sub>2</sub>, WSi<sub>2</sub> and ReSi<sub>1.75</sub> in which each metal oxide possesses an appreciably high vapor pressure, a complete SiO<sub>2</sub> scale can be formed when the vapor pressure reaches 10 Pa. The temperature at which the evaporation pressure of WO<sub>3</sub> reaches 10 Pa was estimated to be about 1500K, about 1100 K for MoSi<sub>2</sub> and about 500 K for ReSi<sub>1.75</sub>.

From the results described above, it is concluded that the disilicides such as MoSi<sub>2</sub>, WSi<sub>2</sub> and ReSi<sub>1.75</sub> take a route B at high temperatures and take a oxidation route C at low temperatures.

(2) Disilicide in which affinity of Si for oxygen is relatively close to that of metal

In oxidation of the disilicides belonging to this category, taking a route C can be expected. In fact, NbSi<sub>2</sub> formed a thick oxide scale consisting of mixed oxides of Nb<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub>. Also in TaSi<sub>2</sub>, similar mixed oxide scale was formed.

(3) Disilicide in which affinity of Si for oxygen is lower than that of metal

In oxidation of the disilicides belonging to this category, taking a oxidation route D, E, or F can be expected. It was found that VSi<sub>2</sub> took a route F at temperatures lower than 1173 K and a route E at temperatures higher than 1173 K. According to literature[7-9], TiSi<sub>2</sub> and ZrSi<sub>2</sub> formed an oxide scale consisting of TiO<sub>2</sub> or ZrO<sub>2</sub> and SiO<sub>2</sub>, namely, these disilicides took a route F.

The oxide scale structures formed on various disilicides are tabulated in Table 1. In the table, serviceable temperature for each disilicide, which was predicted from oxide scale structure, is also shown.

Table 1 Structure of oxide scale on disilicide and oxidation resistance.

Oxide scale structure	Silicide	Oxid. resistance	Temp. region
SiO <sub>2</sub> scale	FeSi <sub>2</sub>	⊙	<1273K
	CoSi <sub>2</sub>	⊙	<1273K
	MoSi <sub>2</sub>	⊙	>1073K
	WSi <sub>2</sub>	⊙	>1573K
	VSi <sub>2</sub>	○	>1173K
	ReSi <sub>1.75</sub>	△	>1273K
	ReSi <sub>1.75</sub>	×	<1273K
Double layer scale	CrSi <sub>2</sub>	⊙	<1373K
		×	>1473K
Mixed oxide scale	NbSi <sub>2</sub>	×	<1773K
	TaSi <sub>2</sub>	×	<1773K
	MoSi <sub>2</sub>	×	773–1073K
	WSi <sub>2</sub>	×	1073–1573K
	VSi <sub>2</sub>	○	<1173K
	TiSi <sub>2</sub>	×	>773K
	Ti <sub>5</sub> Si <sub>3</sub>	×	>773K

⊙ Excellent      ○ Good      △ poor      × very poor

## Summary

In the present study, structures of oxide scales formed on various disilicides were observed. The oxide scales formed on disilicides could be grouped into 3 types, (a) silica scale, (b) mixed oxide (silica+metal oxide) scale, and (c) double layered (silica/metal oxide) scale. Disilicides that form an oxide scale of the type of (a) generally show excellent oxidation resistance. As such disilicides, there were FeSi<sub>2</sub>, CoSi<sub>2</sub>, MoSi<sub>2</sub>, WSi<sub>2</sub>, etc. In FeSi<sub>2</sub> and CoSi<sub>2</sub> (oxidation route A), a protective silica scale was formed due to the selective oxidation of Si, whereas as in MoSi<sub>2</sub> and WSi<sub>2</sub> (oxidation route B) evaporation of metal oxide played an important role for the formation of a silica scale. TaSi<sub>2</sub> and NbSi<sub>2</sub> (oxidation route C) belonged to the type (b) and only CrSi<sub>2</sub> the type (c). Oxidation processes of these disilicides were also discussed.

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