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 $FeSi_2$, $CoSi_2$, $MoSi_2$, WSi_2, etc. In $FeSi_2$ and $CoSi_2$, a protective silica scale must be formed due to the selective oxidation of Si, whereas in $MoSi_2$ and WSi_2 evaporation of metal oxide plays an important role for the formation of a silica scale. Oxidation of $TaSi_2$ and $NbSi_2$ belonged to the type (b), and only $CrSi_2$ the type (c).

Introduction

Disilicides such as $MoSi_2$ 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 $MoSi_2$ [1-3] and WSi_2 [4,5], show excellent oxidation resistance at high temperatures. This is due to the formation of a protective 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 $FeSi_2$, $CoSi_2$, $MoSi_2$, WSi_2, $CrSi_2$, $NbSi_2$, $TaSi_2$, VSi_2, and $ReSi_{1.75}$, 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 Archimedean 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 μm 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:

$$2x\cdot MeSi_2 + (8x+1)\cdot O_2 \rightarrow 2Me_xO + 4x\cdot SiO_2 \quad (1)$$

$$y\cdot MeSi_2 + (2y-1)\cdot O_2 \rightarrow Me_ySi + (2y-1)\cdot SiO_2 \quad (2)$$

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.

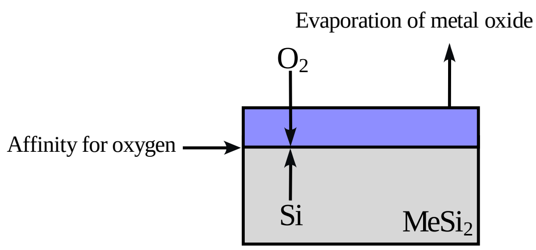


Fig.1 Thermodynamic and kinetic factors in oxidation of dislicide.

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: $FeSi_2$, $CoSi_2$, $MoSi_2$, WSi_2, $ReSi_{1.75}$. In these disilicides, it is speculated that Si tends to be selectively oxidized, leading to formation of a SiO_2 scale.

(b) Affinity of Si for oxygen is relatively close to that of metal: $NbSi_2$, $TaSi_2$, $CrSi_2$. 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: VSi_2, $TiSi_2$, $ZrSi_2$. 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 SiO_2 scale, is required for continuous growth of a 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 SiO_2 scale is liable to occur.

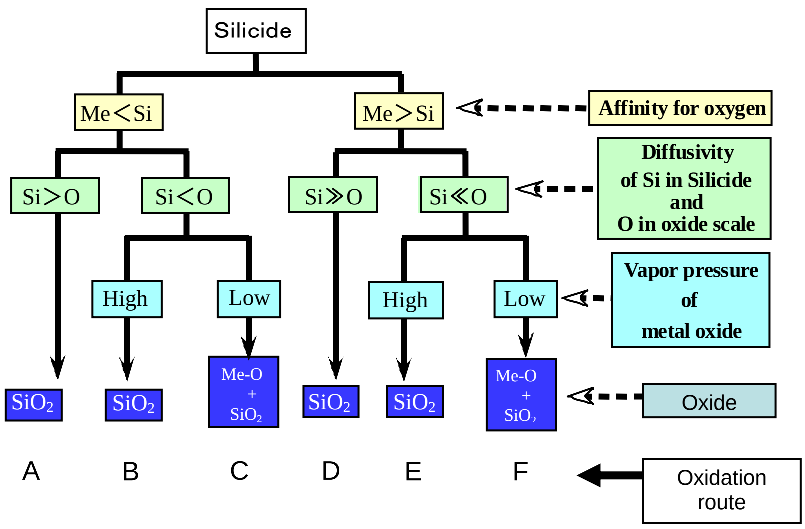


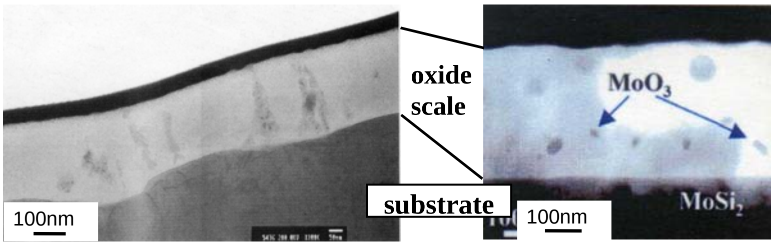
Fig. 2 Prediction of oxidation route in disilicides.

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_2 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_2 scale. That is to say, only SiO_2, 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_3, WO_3, and Re_2O_7 are appreciably high, and the high vapor pressure is particularly advantageous for forming a SiO_2 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.



(a) $CoSi_2$ (b) $MoSi_2$

Fig. 3 TEM photographs of oxide scales formed on (a) $CoSi_2$ for 360ks at 1373 K and(b) $MoSi_2$ 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 $CoSi_2$ at 1373 K and $MoSi_2$ at 1273 K in air. It can be understood that each disilicide forms a SiO_2 scale almost completely at the oxidation temperature.

Structures of all oxide scales formed on $CoSi_2$ in a temperature range of 773 K to 1373 K were similar to that in Fig. 3(a). $FeSi_2$ also forms a complete SiO_2 scale in a temperature range of 773 K to 1273 K. Here, as maximum oxidation temperature for $CoSi_2$ and $FeSi_2$ 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 $CoSi_2$ and $FeSi_2$ demonstrates that Si is selectively oxidized to form a SiO_2 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 $CoSi_2$ and $FeSi_2$ takes a route A.

On the other hand, $MoSi_2$ and WSi_2 form a complete SiO_2 layer at temperatures higher than 1273 K and 1573 K, respectively, but these disilicides form a mixed oxide scale consisting of SiO_2 and metal oxide (MoO_3 or WO_3) at lower temperatures. An example of the oxide scale structure is demonstrated in Fig. 4 which shows the oxide scale formed on $MoSi_2$ at 773 K. The oxide scale consists of an amorphous

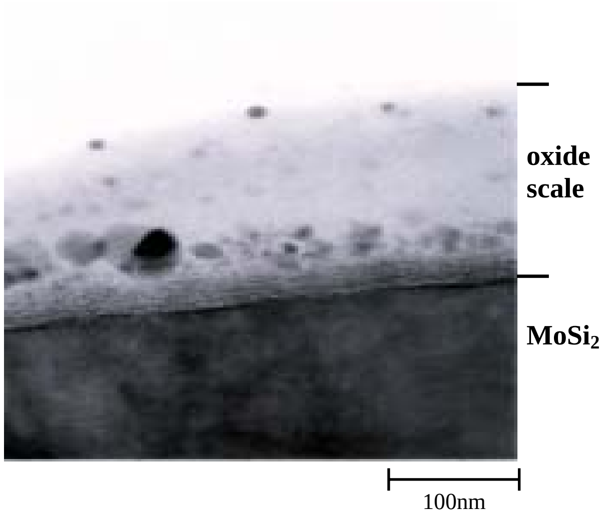


Fig. 4 TEM photograph of oxide scale formed on $MoSi_2$ for 360 ks at 773 K.

SiO_2 scale containing a number of fine MoO_3 particles. Similarly, WSi_2 also forms an mixed oxide scale consisting of SiO_2 and WO_3 in a low temperature region, as shown in Fig. 5. It can be seen in Fig. 5 that the oxide scales formed on WSi_2 are grouped into 3 types, depending on oxidation temperature. At temperatures below 1073 K, the oxide scales consist of the mixed oxides of WO_3 and SiO_2. In the intermediate temperature range, oxide scales having double-layer structure are formed. The outer and inner layers are consisting of SiO_2 and the mixed oxides of WO_3 and SiO_2, respectively. At temperatures above 1573 K, an oxide scale consisting of only SiO_2 is formed. The formation of the outer SiO_2 layer in the intermediate temperature range must be caused by evaporation of WO_3. In other words, evaporation of WO_3 plays an important role for the formation of a complete SiO_2 layer.

At the moment when WSi_2 is exposed to an oxidizing atmosphere, W and Si must be simultaneously oxidized to form WO_3 and SiO_2. In the case that the vapor pressure of WO_3 is appreciably high, it is expected that only SiO_2 is liable to be left on the substrate. In fact, the oxide scales formed at temperatures above 1573 K consisted of only SiO_2. Once the substrate is covered with a protective SiO_2 scale, only SiO_2 grows in further oxidation. In other words, selective oxidation occurs. However, at lower temperatures, the evaporation rate was not enough to left only SiO_2. Therefore, WSi_2 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_2 scale can be estimated. Our recent study on some disilicides demonstrated a clear relationship between vapor pressure

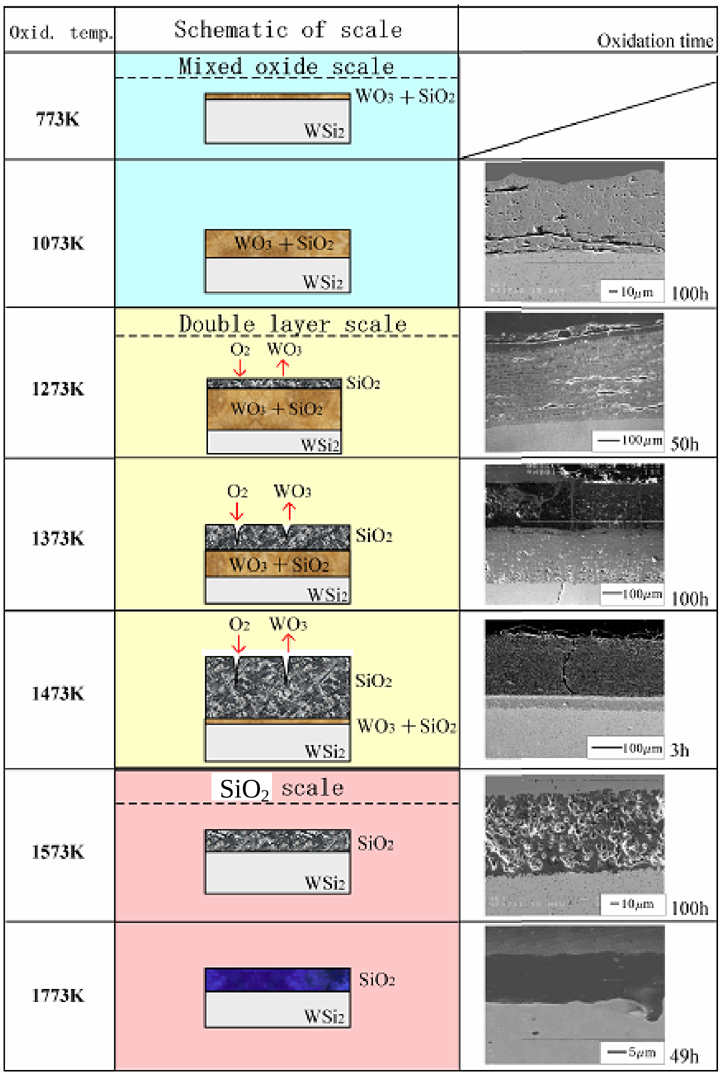


Fig. 5 Cross-sectional SEM photographs of oxide scales formed on WSi_2 at various temperatures.

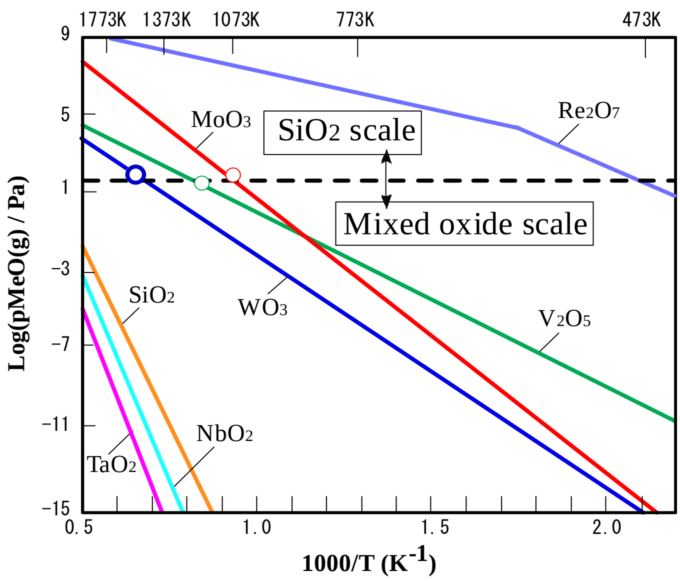


Fig. 6 Vapor pressure of various metal oxides.

of a metal oxide and formation of a SiO_2 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_2 scale. In $MoSi_2$, WSi_2 and $ReSi_{1.75}$ in which each metal oxide possesses an appreciably high vapor pressure, a complete SiO_2 scale can be formed when the vapor pressure reaches 10 Pa. The temperature at which the evaporation pressure of WO_3 reaches 10 Pa was estimated to be about 1500K, about 1100 K for $MoSi_2$ and about 500 K for $ReSi_{1.75}$.

From the results described above, it is concluded that the disilicides such as $MoSi_2$, WSi_2 and $ReSi_{1.75}$ 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, $NbSi_2$ formed a thick oxide scale consisting of mixed oxides of Nb_2O_5 and SiO_2. Also in $TaSi_2$, 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_2 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], $TiSi_2$ and $ZrSi_2$ formed an oxide scale consisting of TiO_2 or ZrO_2 and SiO_2, 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_2 scale	$FeSi_2$	◎	＜1273K
	$CoSi_2$	◎	＜1273K
	$MoSi_2$	◎	＞1073K
	WSi_2	◎	＞1573K
	VSi_2	○	＞1173K
	$ReSi_{1.75}$	△	＞1273K
	$ReSi_{1.75}$	×	＜1273K
Double layer scale	$CrSi_2$	◎	＜1373K
		×	＞1473K
Mixed oxide scale	$NbSi_2$	×	＜1773K
	$TaSi_2$	×	＜1773K
	$MoSi_2$	×	773－1073K
	WSi_2	×	1073－1573K
	VSi_2	○	＜1173K
	$TiSi_2$	×	＞773K
	Ti_5Si_3	×	＞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 $FeSi_2$, $CoSi_2$, $MoSi_2$, WSi_2, etc. In $FeSi_2$ and $CoSi_2$ (oxidation route A), a protective silica scale was formed due to the selective oxidation of Si, whereas as in $MoSi_2$ and WSi_2 (oxidation route B) evaporation of metal oxide played an important role for the formation of a silica scale. $TaSi_2$ and $NbSi_2$ (oxidation route C) belonged to the type (b) and only $CrSi_2$ the type (c). Oxidation processes of these disilicides were also discussed.

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