Formation of SiO$_2$ Scale in High-Temperature Oxidation of WSi$_2$[†]

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Abstract

In order to clarify the relationship between evaporation of WO$_3$ and formation of a SiO$_2$ scale in WSi$_2$, high temperature oxidation tests of WSi$_2$ were carried out at the temperature range from 773 to 1773 K in air. The pronounced effect of the evaporation of WO$_3$ on the structure of oxide scale was found at temperatures higher than 1273 K, and a protective SiO$_2$ scale was formed above 1573 K. The requisite evaporation rate and the vapor pressure of WO$_3$ for the formation of a protective SiO$_2$ scale were estimated to be about 10^{-4} kgm^{-2}s^{-1} and 10 Pa, respectively.

KEY WORDS: (WSi$_2$) (High-Temperature Oxidation) (Evaporation of WO$_3$), (Structure of Oxide Scale) (SiO$_2$ Scale)

1. Introduction

It is well known that some refractory metal disilicides, for example MoSi$_2$ and WSi$_2$, show excellent oxidation resistance at high temperatures, due to the formation of a protective SiO$_2$ scale. In addition, they have a high melting point. Therefore, they are being considered as promising materials for applications at ultra-high temperatures in oxidizing environments.

When metal oxide(s) formed on a metal disilicide possess high vapor pressure(s), it is speculated that evaporation of the metal oxide plays an important role in formation of a protective 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 metal disilicide. In fact, it is known that MoSi$_2$ [1-2], WSi$_2$ [3] and ReSi$_{1.75}$ [4] form a protective SiO$_2$ scale at high temperatures. The vapor pressures of MoO$_3$, WO$_3$, and Re$_2$O$_7$ are appreciably high, and the high vapor pressure is particularly advantageous for forming a SiO$_2$ scale. However, a relationship between evaporation of metal oxide and formation of a SiO$_2$ scale has not yet been clarified.

In the present study, high temperature oxidation tests of WSi$_2$ were carried out in the temperature range from 773 to 1773 K in air, and a relationship between evaporation of WO$_3$ and formation of a SiO$_2$ scale in WSi$_2$ was clarified.

2. Experimental

Fully-dense WSi$_2$ specimens were fabricated by a spark plasma sintering method. In this method, WSi$_2$ powder (average grain size: 2.49 micrometer) was sintered at 1723 K. For the sintering, a high heating rate of 10 K/min was applied. The average grain size in the sintered WSi$_2$ was about 25 micrometer and the bulk density was 95 % of the theoretical value.

Specimens for oxidation tests were cut into about 8x3x1 mm pieces from the sintered WSi$_2$. The surfaces were polished to a 1 micrometer diamond finish, and then cleaned ultrasonically in ethanol.

Oxidation tests of the WSi$_2$ specimens were carried out at temperatures ranging from 773 to 1773 K in air. The mass change by oxidation was automatically measured by a thermobalance. The oxidized specimens were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and electron probe microanalyser (EPMA).

3. Results
3.1 Oxidation behavior

Figure 1 shows oxidation kinetics of WSi$_2$ at temperatures ranging from 773 to 1773 K in air. The mass change by oxidation depends strongly on temperature. To make clear the temperature dependence, the mass change for 100 hr is shown in **Fig. 2**. In the temperature range from 773 to 1273 K, the mass gain increases with temperature and reaches a maximum value at 1273 K. In
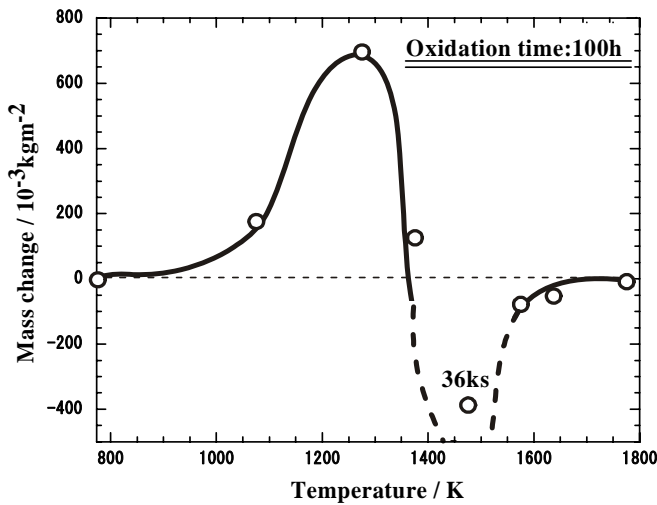
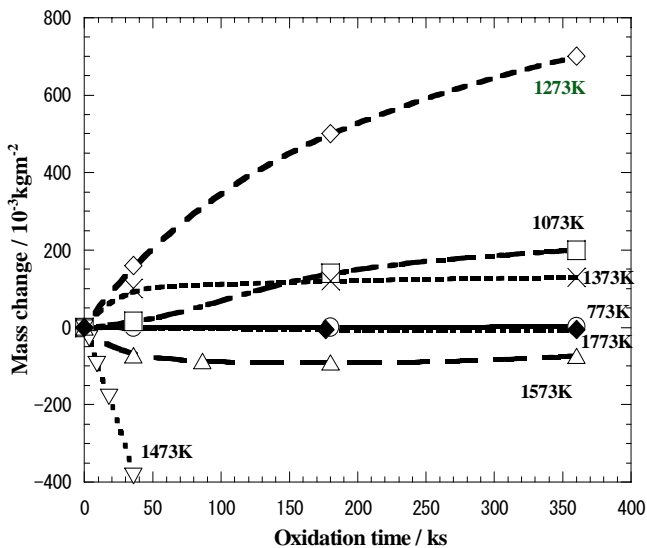**Fig. 1** Oxidation kinetics of WSi$_2$ in air.

Fig. 2 Temperature dependence of mass change for 100 hr.

the higher temperature region, especially at 1473 K, great mass loss takes place. This may be due to the evaporation of W oxide (WO$_3$). On the other hand, at higher temperatures than 1573 K the mass change becomes negligibly small.

3.2 Scale structure

To understand the oxidation behavior of WSi$_2$, the oxide scales formed on it at various temperatures were observed. According to X-ray analysis, the oxide scales formed at temperatures below 1073 K consisted of mixed oxides of SiO$_2$ and WO$_3$. On the other hand, the oxide scales formed at temperatures above 1573 K consisted of SiO$_2$ only.
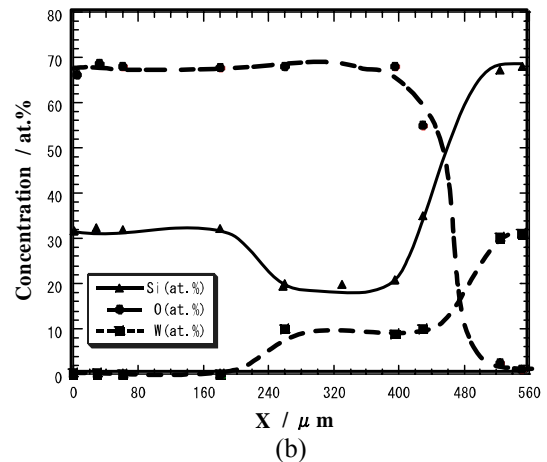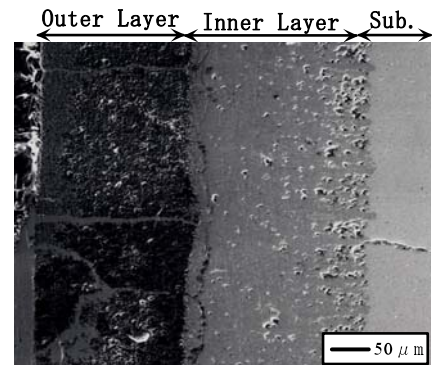

(b)

Fig. 3 SEM photographs (a) and concentration profiles (b) in the cross-section of the scale formed on WSi$_2$ for 100 hr at 1373 K.

In the intermediate temperature region (1273-1473 K), a characteristic scale structure, namely a double layer structure, was observed. **Figure 3** shows SEM photographs and concentration profiles in the cross-section of the scale formed on WSi$_2$ for 100 hr at 1373 K. The oxide scale consists of two layers: outer and inner. The inner layer consists of the mixed oxides of SiO$_2$ and WO$_3$, and the atomic ratio of Si to W is almost constant at 2 throughout the layer. On the other hand, the outer layer consists of SiO$_2$. The structures of the scales formed at temperatures below 1073 K were similar to that of the inner layer formed at 1373 K.

Based on observation of the oxide scales, the scale structure is schematically summarized in **Fig. 4**. Formation of the double-layer structure is observed at temperatures above 1273 K, and only SiO$_2$ remains on scale increases with temperature, but a protective SiO$_2$ layer is formed at temperatures beyond 1573 K.

4. Discussion
4.1 Oxidation mechanism

In oxidation of disilicides, selective oxidation of Si or simultaneous oxidation of metal and Si could be observed.
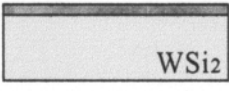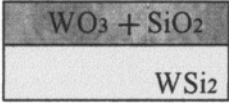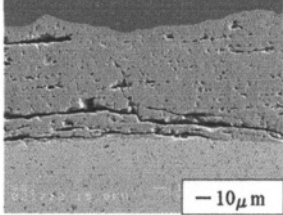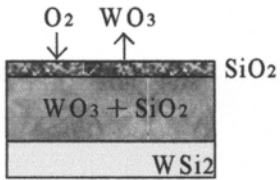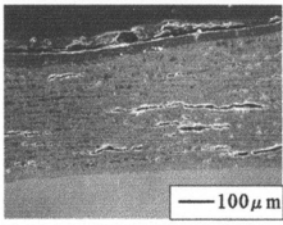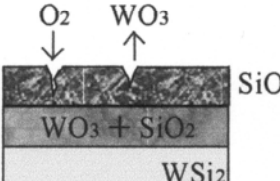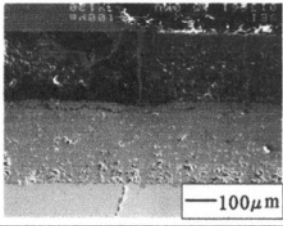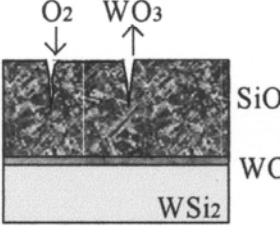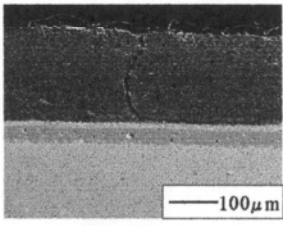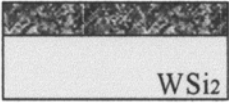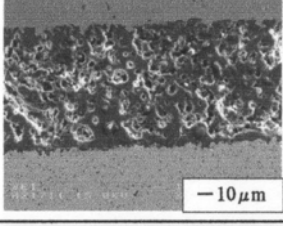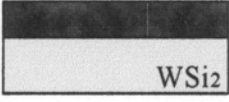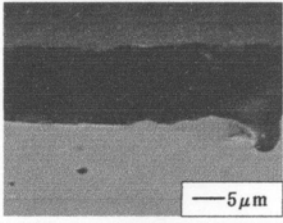
Temp.	Scale structure	Oxidation time
773K	$WO_3 + SiO_2$ / WSi_2	
1073K	$WO_3 + SiO_2$ / WSi_2	$-10\mu m$ 100h
1273K	O_2 ↓ WO_3 ↑ / SiO_2 / $WO_3 + SiO_2$ / WSi_2	$-100\mu m$ 50h
1373K	O_2 ↓ WO_3 ↑ / SiO_2 / $WO_3 + SiO_2$ / WSi_2	$-100\mu m$ 100h
1473K	O_2 ↓ WO_3 ↑ / SiO_2 / $WO_3 + SiO_2$ / WSi_2	$-100\mu m$ 3h
1573K	SiO_2 / WSi_2	$-10\mu m$ 100h
1773K	SiO_2 / WSi_2	$-5\mu m$ 49h

Fig. 4 Schematic diagram of the structure of scales formed on WSi_2.

Thus, the oxidation reactions are expressed as follows:

$$2xMeSi_2 + (8x+1)O_2 \rightarrow 2Me_xO + 4xSiO_2 \qquad (1)$$

$$yMeSi_2 + (2y-1)O_2 \rightarrow Me_ySi + (2y-1)SiO_2 \qquad (2)$$

Which reaction is liable to occur depends on thermodynamic (affinity of metal and silicon for oxygen) and kinetic (diffusivity of oxygen in oxide scale and silicon in disilicide) factors. Therefore, these factors must be considered for understanding oxidation mechanism of disilicides [5]. Moreover, in the case that the metal oxide possesses a high vapor pressure, the evaporation must be considered. Namely, when the metal oxide(s) formed on a disilicide possess high vapor pressure(s), it is speculated that evaporation of the metal oxide plays an important role in formation of a SiO₂ scale. The detail will be stated below.

Based on the present results of the oxidation behavior and the scale structures in oxidation of WSi₂, an oxidation mechanism can be proposed. When WSi₂ is exposed to an oxidizing atmosphere, W and Si must be simultaneously oxidized to form WO₃ and SiO₂ in the early stage of oxidation. At low temperatures, the mixed oxide scale grows as it is. On the other hand, at higher temperatures, because of the high vapor pressure of WO₃, it is evaporated from the oxide scale. Consequently, only SiO₂ is liable to be left on the substrate. In fact, the scales formed at temperatures above 1573 K consisted of only SiO₂. Once the substrate is covered with a protective SiO₂ scale, only SiO₂ grows during further oxidation. In other words, selective oxidation occurs.

Thus, the oxide scales formed on WSi₂ are grouped into 3 categories, depending on oxidation temperature. At low temperatures below 1073 K, the scales consist of the mixed oxides of WO₃ and SiO₂. At high temperatures above 1573 K, a scale consisting of SiO₂ is formed. In the intermediate temperature range, scales having double-layer structures are formed. The outer and inner layers consist of SiO₂ and the mixed oxides of WO₃ and SiO₂, respectively. The formation of the outer layer must be due to evaporation of WO₃. Based on such structures of scale formed in the intermediate temperature region, the requisite evaporation rate and vapor pressure of WO₃ for the formation of a SiO₂ scale are discussed in next sections.

4.2 Requisite evaporation rate of WO₃ for formation of entire SiO₂ scale

Based on the thickness of the outer layers formed at 1273, 1373, and 1473 K, estimation of the evaporation rate of WO₃ is as given below.

WO₃ of 1 mole and SiO₂ of 2 mole are simultaneously produced in the oxidation of WSi₂, but the evaporation of WO₃ leads to the formation of the outer layer (thickness d /m) consisting of SiO₂ from the evaporation of WO₃. Then, the evaporation rate per unit volume (v /kgm⁻²s⁻¹) is given as follows:

$$v = [V_{WO} / (V_{WO} + 2V_{SO})] \cdot \rho_{WO} \cdot d \cdot 1/t . \qquad (3)$$

V_{WO} and V_{SO} (m³) are volumes of WO₃ and SiO₂ making up the mixed oxide scale of unit volume, respectively, ρ_{WO} (kgm⁻³) density of WO₃, and t (s) oxidation time.

Although the evaporation rate somewhat decreased with oxidation time, the rate at an early stage of oxidation at each temperature is shown as a function of reciprocal temperature in **Fig. 5**. In this figure, the requisite evaporation rates of WO₃, v', for the formation of a scale consisting of entire SiO₂ are also shown. The rate was estimated from the whole thickness of the oxide scale formed at each temperature. The point of intersection of the two straight lines (about 1500 K) may indicate the minimum temperature that is necessary for the formation of an entire SiO₂ scale.
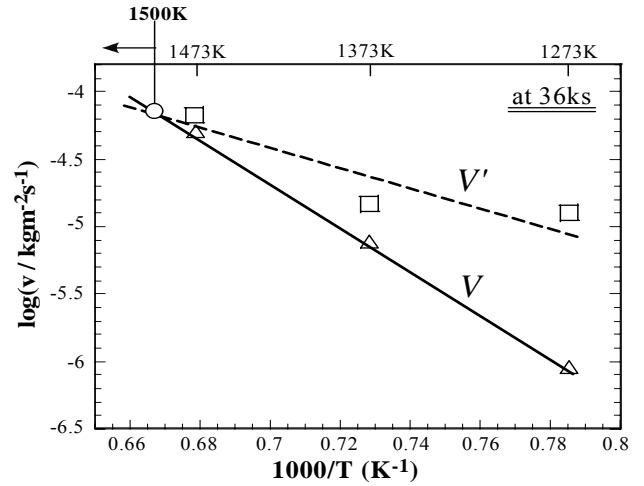
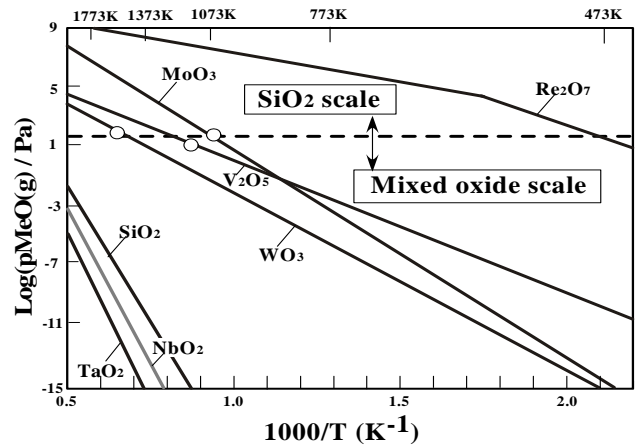**Fig. 5** Arrhenius plot of estimated evaporation against 1/ T.

Fig. 6 Vapor pressures of metal oxides rate of WO₃.

4.3 Requisite vapor pressure of WO$_3$ for formation of entire SiO$_2$ scale

According to our previous study [4], a clear relationship between vapor pressure of a metal oxide and formation of a SiO$_2$ scale was recognized. The relationship can be understood from **Fig. 6**, where open circles indicate the transition temperatures from the formation of a double layer scale to that of a SiO$_2$ scale. In some metal disilicides, an entire SiO$_2$ scale can be formed when the vapor pressure of the metal oxide reaches 10 Pa. The temperature where the evaporation pressure of WO$_3$ reaches 10 Pa is estimated to be about 1500K. This estimated temperature is in good agreement with that recognized from the scale structure shown in Fig.4.

5. Conclusion

In order to clarify the effect of the evaporation of metal oxide on the formation of a protective SiO$_2$ scale, oxidation tests of WSi$_2$ were carried out. The conclusions obtained in the present study are summarized as follows.

(1) The oxidation behavior of WSi$_2$ is strongly affected by the evaporation of WO$_3$.

(2) A pronounced effect of the evaporation of WO$_3$ on the formation of a SiO$_2$ scale is found at temperatures higher than 1273 K.

(3) The requisite evaporation rate and vapor pressure of WO$_3$ for the formation of an entire SiO$_2$ scale are about 10^{-4} kgm^{-2}s^{-1} and 10 Pa, respectively.

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