Degradation of Yb–Gd–Ti-Si middle entropy silicides in oxidizing atmosphere

Yutaro Arai 1 and Ryo Inoue 2

1 Department of Materials Science & Technology, Tokyo University of Science, 6–3–1, Niiyuku, Katsushika-ku, Tokyo, 125–8585, Japan
2 Department of Mechanical Engineering, Tokyo University of Science, 6–3–1, Niiyuku, Katsushika-ku, Tokyo, 125–8585, Japan

E-mail: inoue.ryo@rs.tus.ac.jp

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Abstract

Using arc melting, a novel rare-earth silicide, middle entropy Yb–Gd–Ti-Si, was fabricated for high-temperature material applications. The oxidation behavior of the Yb–Gd–Ti-Si was evaluated through oxidation tests conducted at 1200 °C for 1, 2, 4, and 8 h in air. The oxidation rate at 1200 °C was almost the same, regardless of the addition of Ti. The oxidation rate of Yb–Gd–Ti-Si at lower temperatures (600 °C to 900 °C) was lower than that of Yb–Gd–Si. In addition, detailed microstructural observations indicate that the formation of TiO2 and other oxides in the Yb–Ti–O (Yb–Ti–Si–O) phase suppresses the formation of Yb2O3, causing a drastic oxidation at intermediate temperatures (600 °C to 900 °C). These results indicate that the addition of Ti to Yb–Gd–Si is effective at preventing the preferential oxidation of the grain boundaries at 600 °C to 900 °C, which is commonly observed in metal silicides.

1. Introduction

Transition metal silicides (e.g., MoSi2, CrSi2, ZrSi2, and NbSi2) have been used as high-temperature materials in oxidizing atmospheres owing to the formation of SiO2 scales on their surfaces (at temperatures of ≥1000 °C), which prevent further oxidation [1–10]. At temperatures of <1000 °C, drastic oxidation with the formation of metal oxides occurs in the absence of SiO2 scales. For example, MoSi2 forms SiO2 scales even at above 1400 °C, and the oxidation rate is relatively low in air (7.06 × 10–14 m2 s–1). [2] At temperatures between 600 °C and 900 °C, a drastic oxidation of MoSi2 proceeds owing to the preferential oxidation of the grain boundaries, which prevents MoSi2 from maintaining its form through complete oxidation. However, the oxidation behavior of MoSi2 at intermediate temperatures improves with the addition of B, Al, Ti, Ta, Zr, and Y because the value of Gibbs-free energy of the oxide formation at 600 °C to 900 °C is lower than that of Si, preventing the preferential oxidation of the grain boundaries [4, 5, 11].

In addition to transition metal silicides, rare-earth silicides have also been studied as coating materials in aero gas turbine engines [12–15]. Such use is due to the oxidation of a conventional coating material (Si) in a combustion environment (T < 1300 °C, 10–30 atm [16]), forming cristobalite, which is a polymorphous type of SiO2, thereby causing the delamination of the coating. Recent preliminary results demonstrated the high-temperature oxidation of ytterbium silicides (Yb2Si5 and Yb2Si3) at up to 1200 °C in both air and steam [15]. The preferential oxidation of Yb prevents the formation of SiO2 and protects it from further oxidation, forming Yb2O3, Yb2SiO5, and Yb2Si3O7. However, the Yb2Si5 and Yb2Si3 phases are unstable because the Si–Yb3Si5 eutectic phase (at a melting temperature of 1125 °C) evolves during oxidation, which is caused by a decrease in the Yb content in these silicides. Specifically, the rapid weight gain and formation of Yb2O3 (at between 700 °C and 900 °C), caused by the preferential oxidation of Yb, is still a critical stability issue.

Because compounds in Gd–Si systems also have higher melting points than Si, Morigayama et al studied the phase stability of Yb25Gd20Si55 ternary silicides at high temperatures (≥1500 °C) using a calculated phase diagram (CALPHAD) to improve the phase stability [17]. The results proved that the addition of Gd prevents oxidation, and the Yb–Si phase stability improves because no liquid phase is formed and the weight gain is...
suppressed at up to ~1200 °C [17, 18]. However, at between 700 °C and 900 °C, a rapid weight gain has been observed owing to the formation of Yb2O3, leading to the preferential oxidation of the grain boundaries, which is still a critical issue in Yb-silicides and Yb–Gd–Si systems. The prevention of oxidation at 700 ~ 900°C is one of the most important challenges to design Yb-silicides and Yb–Gd–Si as a candidate of coating materials in aero gas turbine engines. However, the reports on the improvement of oxidation behavior of them is limited to the best of the author’s knowledge.

The objective of this study is to improve the oxidation behavior of a Yb–Gd–Si ternary system at low temperatures. In this research, Ti was added to Yb–Gd–Si to improve the oxidation behavior of silicides and ceramics (e.g., MoSi2 and Ni-based superalloys) [9, 16]. This is mainly because the value of Gibbs’ free energy for the oxidation of Ti is lower than that of Si and Ni, which causes the preferential oxidation of Ti and prevents the oxidation of the grain boundaries. In addition, as the entropy of the mixture increases, thermodynamic oxidation is expected to decrease.

2. Experimental

2.1. Materials and methods

Yb–Gd–Ti–Si was fabricated using an arc-melting furnace. In addition, Yb (99.9% purity, Mitsui Kinzoku Trading Co. Ltd, Japan), Gd (99.9% purity, Mitsui Kinzoku Trading Co. Ltd, Japan), Ti (99.9% purity, Nirako Co. Ltd, Japan), and Si (99.9% purity, Kojundo Chemical Co., Japan) granules were used as the raw materials. Granular mixtures of Yb:Gd:Ti:Si with relative proportions of 30:14:5:55 (at%) and 30:14:1:55 (at%) were prepared (which are hereafter denoted as Yb30Gd14.5Ti5Si and Yb30Gd14Ti1Si, respectively). The compositions were determined from the phase diagram of Yb–Gd–Si using CALPHAD (FactSage 7.3, Centre for Research in Computational Thermochemistry, Canada) with a melting point of ≥ 1500 °C. Yb30Gd14.5Ti5Si and Yb30Gd14Ti1Si were prepared by arc-melting methods. First, granular mixture of them were put onto arc-furnace. To avoid oxidation during process, evacuation and the introduction of Ar is repeated by three times. After that, arc-furnace was filled with Ar with the pressure of ~0.06 atm. Owing to the rapid evaporation of Yb in an inert atmosphere, arc melting was repeated four times with the addition of Yb. A similar description of the preparation process can be also found in our previous report [17].

The microstructure and composition of the samples were characterized using electron microscopy (SEM; JSM-6510SA, JEOL, Japan) equipped with x-ray energy dispersive spectroscopy (EDX). To study the structural properties, x-ray diffraction (XRD) using a MiniFlex 600 Rigaku, Japan) was carried out within the 2θ range of 20°–80° using CuKα radiation (at a wavelength of 0.154 nm). Furthermore, using the intercept method, the surfaces of the samples were etched using aqua regia to evaluate the mean grain size. Since quantitative determination of crystallite was quite difficult in the present study, analyses for grain size were conducted. The grain size can be estimated using the mean linear intercept length ($l$), which is expressed through the following equation:

$$l = \frac{L}{n_l}$$

where $L$ and $n_l$ represent the length of a line drawn in a micrograph and the number of grains intersecting that line, respectively. The area of the grain boundaries ($S_v$) is then calculated using $l$ as follows:

$$S_v = \frac{2}{l}$$

2.2. Oxidation tests

To evaluate the oxidation rates, the samples (6.0 mm × 6.0 mm × 4.0 mm) were exposed to air at 1200 °C for 1, 2, 4, and 8 h in an infrared (IR) furnace (IR-QP1-4S, Yonekura MFG Co., Ltd, Osaka, Japan). To avoid oxidation while reaching the desired temperature, a flow of Ar (500 ml min⁻¹) was used to maintain an inert atmosphere. After reaching 1200 °C, the Ar flow was closed and air was introduced at a rate of 500 ml min⁻¹. After the test time at 1200 °C, the air flow was stopped, the Ar flow (500 ml min⁻¹) was reinitiated to prevent further oxidation, and the samples were cooled to room temperature (25 °C) at a cooling rate of ~50 °C min⁻¹. The detailed conditions of the heat-exposure test using an IR furnace can be found in [17]. Additional oxidation tests were conducted to evaluate the oxidation of the samples at lower temperatures. The samples were heated to 700 °C and 900 °C at a heating rate of 50 °C min⁻¹, and after reaching 700 °C or 900 °C, the samples were cooled to room temperature at a cooling rate of ~50 °C min⁻¹. After each test, the heat-exposed samples were embedded in an epoxy resin to observe their cross-sections. The microstructures were observed and characterized using SEM. The oxidized region was measured by using image processing software (Image J, NIH) from cross-sectional images. To evaluate the crystal structures of the samples, an XRD analysis was conducted under the same conditions as those mentioned above. In addition, the
weight gain of the samples during heat exposure was measured through a thermogravimetric analysis (TGA) using a Netzsch 2000 SE-a (Netzsch, Germany) with a uniform weight of ∼10 mg, and the samples were heated to 1200 °C at a heating rate of 5 °C min⁻¹.

3. Results and discussion

3.1. Microstructures of Yb–Gd–Ti–Si
The backscattered electron (BSE) images of the Yb₃₀Gd₁₄.₅Ti₀.₅Si and Yb₃₀Gd₁₄Ti₁.₅Si microstructures are shown in figures 1(a) and (b), respectively. Three different regions of contrast are shown: bright, gray, and dark. Bright and gray regions were also previously observed in Yb–Gd–Si by Morigayama et al and represent the Yb₂O₃ (impurities formed during arc melting) and Yb–Gd–Si phases, respectively. [17] A detailed observation of the gray region reveals the presence of a brighter gray region (P1 in figure 1(c)) and a darker gray region (P2 in figure 1(c)), which indicates a two-phase region. The EDX map and point analysis of these regions (see figure 1(c) and table 1) indicate two Yb–Gd–Si phases, with the Yb, Gd, and Si contents within the range of 15–30, 10–30, and 50–65 at%, respectively. These results were expected because Yb–Gd–Si has two stable phases within these compositional ranges. In the EDX map analysis, the darkest randomly distributed regions were attributed to the Ti–Si phases because the signals of Ti and Si overlapped (figure 1(c)). The formation of the Ti–Si phases decreased the Si content in the Yb–Gd–Si phase, which revealed that the melting point decreased, as shown in the Yb–Gd–Si ternary phase diagram (figure 2). However, the melting point of the silicides is ≥1500 °C owing to the relatively low Ti content (0.5–1.0 at%), which indicates that the stability of the Yb₂₀Gd₁₄.₅Ti₀.₅Si and Yb₂₀Gd₁₄Ti₁.₅Si phases is almost the same as that of Yb–Gd–Si. Figure 3 shows the XRD patterns of Yb₃₀Gd₁₄.₅Ti₀.₅Si and Yb₃₀Gd₁₄Ti₁.₅Si. Reference peaks for Yb–Gd–Si and Y₂O₃ is also shown [17, 19]. No significant changes were observed in the XRD patterns upon the addition of Ti. This result was expected because the amount of Ti in the samples (0.5%–1.0%) was much lower than that of Yb, Gd, and Si. Furthermore, to clarify the microstructural changes caused by the addition of Ti, BSE images of the etched surfaces of the Yb–Gd–Si, Yb₂₀Gd₁₄.₅Ti₀.₅Si, and Yb₂₀Gd₁₄Ti₁.₅Si samples and EDX analysis results of Yb, Gd, Si, and Ti are shown in figures 4(a) and (b), respectively. These results suggest a decrease in the number of grains of the samples with an increase in the Ti content. The enlarged views and EDX analysis results clearly show that the Ti–Si phases exhibit intergranular regions. Figures 5(a) and (b) show I and Sᵣ, respectively. The value of I for both Yb–Gd–Si and Yb₂₀Gd₁₄.₅Ti₀.₅Si is ∼90 μm. In addition, I for Yb₂₀Gd₁₄Ti₁.₅Si is higher than that of Yb–Gd–Si and

![Figure 1. BSE images of (a) Yb₃₀Gd₁₄.₅Ti₀.₅Si and (b) Yb₃₀Gd₁₄Ti₁.₅Si microstructures and (c) EDX mapping of Yb₂₀Gd₁₄Ti₁.₅Si.]

![Table 1. EDX point analyses for points 1 and 2 in figure 1(b).]

|          | Yb(at%) | Gd(at%) | Si(at%) | Ti(at%) |
|----------|---------|---------|---------|---------|
| P1       | 25.34   | 20.95   | 53.71   | 0       |
| P2       | 20.27   | 25.22   | 54.51   | 0       |

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Figure 2. Yb–Gd–Si phase diagrams (Yb, 0–70 at%; Gd, 0–70 at%; Si, 30–100 at%).

Figure 3. XRD pattern of as-prepared Yb$_{30}$Gd$_{14}$Ti$_{5}$Si.
Figure 4. (a) BSE images of the etched surfaces of the samples and (b) EDX analysis of $\text{Yb}_{x}\text{Gd}_{1-4}\text{Ti}_{1}\text{Si}$ with magnified images.

Figure 5. (a) Mean linear intercept length and (b) grain boundary area per unit volume as a function of Ti content.
Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si, whereas $S_i$ is lower. These results suggest that the grain size of the samples increased with the addition of Ti, and the area of the grain boundaries decreased.

3.2. Oxidation behavior of Yb–Gd–Ti–Si

The TG curves of Yb–Gd–Si, Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si, and Yb$_{30}$Gd$_{14}$Ti$_{1.5}$Si in air are shown in figure 6. The total weight gain during the TG test increased with the addition of Ti, and the rate of weight gain for both silicides was basically the same at above 900 °C (figure 6(a)). However, it seems that the weight gain of Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si and Yb$_{30}$Gd$_{14}$Ti$_{1.5}$Si at intermediate temperatures (∼600°C–900°C) is lower than that of Yb–Gd–Si. The largest difference was observed at between 800 °C and 900 °C. An enlarged view within the range of 850 °C to 900 °C shows that the oxidation rates of Yb–Gd–Si and Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si were within the range of $\sim 1.2 \times 10^{-2}$ and $2.3 \times 10^{-2}$ °C$^{-1}$, whereas that of Yb$_{30}$Gd$_{14}$Ti$_{1.5}$Si was $\sim 9.9 \times 10^{-3}$ °C$^{-1}$ (figure 6(b)). These results clearly show that the oxidation rate decreases with an increase in the Ti content at 600 °C to 900 °C. This implies that the addition of Ti suppresses the formation of Yb$_2$O$_3$ during oxidation. BSE images along with EDX analyses for Yb–Gd–Si [17] and Yb$_{30}$Gd$_{14}$Ti$_{1.5}$Si after oxidation at 1200 °C for both 1 and 8 h time frames are shown in figure 7.

For Yb–Gd–Si, the continuous bright contrast region corresponds to Yb$_2$O$_3$, and the other contrast regions represent oxides in the Yb–Gd–Si–O system with different contents of Yb, Gd, and Si, as reported in a literature [17]. A continuous Yb$_2$O$_3$ region appeared above the unoxidized area and below the oxides in the Yb–Gd–Si–O system. In Yb$_{30}$Gd$_{14}$Ti$_{1.5}$Si, a continuous Yb$_2$O$_3$ region was formed in the oxides of the Yb–Gd–Si–O system. In addition, circular Yb$_2$O$_3$ particles were scattered in the unoxidized region. In addition, the Ti–Si phase was clearly observed in the unoxidized region along with the Ti signal in the oxidized region. These microstructural characteristics differ from those of oxidized Yb–Gd–Si. The XRD patterns of Yb–Gd–Si, Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si, and Yb$_{30}$Gd$_{14}$Ti$_{1.5}$Si, along with the patterns of Yb and Gd silicates, are shown in figure 8. Reference patterns for Yb and Gd contained silicates are also exhibited [19]. Similar XRD patterns were obtained after the oxidation of...
Figure 7. BSE images with EDX mapping analysis after oxidation: (a) Yb–Gd–Si after 1 h, (b) Yb–Gd–Si after 8 h, (c) Yb$_{30}$Gd$_{14}$Ti$_{1}$Si after 1 h, and (d) Yb$_{30}$Gd$_{14}$Ti$_{1}$Si after 8 h.

Figure 8. XRD patterns of the samples after oxidation at 1200 °C.
these samples. Although it was difficult to confirm the formation of the TiO$_2$ phase owing to the complex XRD patterns obtained after oxidation, a peak corresponding to the TiO$_2$-based phase was observed in the Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si and Yb$_{30}$Gd$_{14}$Ti$_{1}$Si samples. In addition, the thickness of the oxidized region as a function of time and the half-power of time are shown in figures 9(a) and (b), respectively. The difference in thickness among the Yb–Gd–Si, Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si, and Yb$_{30}$Gd$_{14}$Ti$_{1}$Si samples for each oxidation time was ∼10–30 μm.

Assuming that the oxidation proceeded, the oxygen diffusion through the oxidized region and the oxidized region thickness growth (defined as the oxidation rate $k_p$) are proportional to the half-power of time (figure 9(b)). The oxidation rates of Yb–Gd–Si, Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si, and Yb$_{30}$Gd$_{14}$Ti$_{1}$Si are 18.3, 18.6, and 18.7 μm h$^{-1}$, respectively. The results of the oxidation tests at 1200 °C indicate no significant changes with the addition of Ti. This result is normal because the Ti content in YbGdTiSi was ∼0.5–1.0 at%, and the difference in the entropy of mixing ($S_{mix}$) between Yb–Gd–Si and YbGdTiSi was relatively low (0.17–0.34 J mol$^{-1}$ K$^{-1}$).

The Gibbs-free energy ($\Delta G_r$) of the oxidation reaction is given by the changes in enthalpy ($\Delta H$) and entropy ($\Delta S$), and the temperature ($T$) is expressed as follows:

$$\Delta G_r = \Delta H - T \Delta S$$

$$\Delta S = S_a - S_b$$

where $S_a$ and $S_b$ represent the entropies before and after the reaction, respectively. An increase in $\Delta S_{mix}$ induced an increase in $S_a$, and the absolute value of $\Delta G_r$ decreased. Assuming that the difference in $\Delta S_{mix}$ for the silicides affects $\Delta G_r$, for Yb–Gd–Ti–Si (and Yb–Gd–Si), $\Delta G_r$ decreases by ∼4–5 kJ mol$^{-1}$ compared with that of Yb3Si5 because the weight gain of these silicides at 1200 °C decreases by 2% in comparison with Yb$_3$Si$_5$. Unfortunately, the weight gain and oxidation rate of these silicides depend on the oxides formed on their surfaces, and it is difficult to extract the effect of the mixed entropy on the oxidation behavior. As discussed previously [18], the

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Figure 9. Thickness of the oxidized region as functions of (a) time and (b) the square root of time.
formation of complex oxides containing Yb–Gd–Si–O (and Yb–Gd–Ti–Si–O) acts as a barrier for oxygen diffusion into the unoxidized area, and similar mechanisms have been reported in studies on the oxidation mechanism of mid- and high-entropy materials [20–22].

To clearly understand the effect of Ti on the oxidation behavior of Yb–Gd–Si, an evaluation at temperatures of lower than 1200 °C was necessary. BSE images of Yb₃₀Gd₁₄Ti₁Si with EDX mapping (oxygen) were obtained after oxidation at 700 °C and 900 °C and are presented in figure 10(a). After oxidation at 700 °C, oxides with a thickness of ~10–20 μm were formed on the surface, and oxidation proceeded along the cracks toward the inside of the sample by ~200 μm in the depth direction. The size of the oxidized region increased by 300–400 μm with an increase in the oxidation temperature, and a continuous oxide region with a thickness of ~100 μm was formed on the surface. However, no oxidation along the cracks was observed in the sample after oxidation at 900 °C. An EDX analysis of the samples after oxidation at 700 °C (figure 8(b)) indicates the formation of oxides composed of Yb, Ti, and O near the surface.

Although the Gibbs-free energy for the formation of TiO₂ at 700 °C (~800 kJ mol⁻¹ [23]) is higher than that of Yb₂O₃ (~1000 kJ mol⁻¹), the oxides at a depth of 100 μm were composed of Ti and O. This shows that the formation of TiO₂ prevented the formation of Yb₂O₃ as well as further oxidation at 600 °C to 900 °C, which was observed through the oxidation of Ti-added MoSi₂ [11]. The TiO₂ also prevented the formation of cracks in the samples and oxidation through intergranular corrosion because Ti was present in the intergranular corrosion regions (see figure 3). Moreover, the authors hypothesize that the formation of oxides in the Yb-Ti-O system prevented the formation of Yb₂O₃ because a similar behavior was observed in the Yb-Si-O of the Yb-Si system [15, 24]. In this case, Yb₂SiO₃ and Yb₂Si₂O₇ were formed despite the Gibbs-free energy during the formation of SiO₂ being much higher than that of Yb₂O₃. The formation of silicates is also reported in Yb₂O₃-SiO₂ and Gd₂O₃-SiO₂ system [25]. The oxides formed in the Yb-Ti-O system also prevented the formation of a continuous Yb₂O₃ phase. In addition, the effect of ΔSₘₚ on corrosion at 600 °C to 900 °C was limited because of the contribution of entropy to the Gibbs-free energy, considering that the reaction increases with an increase in temperature, as shown in equation (4). A detailed observation of the cross-sections in figures 10(c) and (d) reveal that complex oxides composed of Yb, Gd, Ti, and Si are formed after oxidation at 900 °C. Detailed thermodynamic and microstructural analyses of complex oxides are required to evaluate the changes in
The oxidation behaviors of mid-entropy silicides Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si and Yb$_{30}$Gd$_{14}$Ti$_{1}$Si were evaluated. The conclusions drawn from this study are as follows.

The oxidation behaviors of Yb–Gd–Si, Yb$_{30}$Gd$_{14.5}$Ti$_{0.5}$Si, and Yb$_{30}$Gd$_{14}$Ti$_{1}$Si at 1200 °C were almost the same. In addition, the weight gain decreased by 2% compared with that of Yb$_3$Si$_5$, suggesting that the addition of Ti to Yb–Gd–Si did not affect the oxidation behavior at 1200 °C.

The oxidation of Yb–Gd–Si at intermediate temperatures (600 °C to 900 °C) was improved by the addition of 1 at% Ti. This occurred mainly because the oxidation rate of Yb$_{30}$Gd$_{14}$Ti$_{1}$Si within the temperature range of 850 °C to 900 °C was $\sim 9.9 \times 10^{-3}$ °C$^{-1}$ and that of Yb–Gd–Si and Yb$_{30}$Gd$_{14}$Ti$_{0.5}$Si was $\sim 1.2$–$2.3 \times 10^{-2}$ °C$^{-1}$. The addition of Ti increased the grain size of the samples, causing the formation of TiO$_2$, leading to the formation of oxides in the Yb–Ti–O system and more complex oxides composed of Yb, Gd, Ti, and Si. As a result, the formation of Yb$_2$O$_3$ was suppressed, and the weight gain decreased at intermediate temperatures.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Yutarō Arai @ https://orcid.org/0000-0001-8062-0637

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