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COMBINED EFFECT OF Zr AND Si ON ISOTHERMAL OXIDATION OF Ti

In this study, the combined effect of Zr and Si on isothermal oxidation of Ti for 25 and 50 h at 820°C, which is the temperature related to exhaust valves operation, was investigated. Si addition into Ti-5mass%Zr alloy led to a distribution of silicide Ti_5Si_3 phase formed by a eutectic reaction. The Ti sample containing only Zr showed more retarded oxidation rate than Ti-6Al-4V, the most prevalent Ti alloy, at the same condition. However, while a simultaneous addition of Zr and Si resulted in greater increase of oxidation resistance. The oxide layer formed after the addition of Zr and Si comprised TiO_2, ZrO_2, and SiO_2.

Keywords: Ti, Zr, Si, silicide, oxidation

1. Introduction

Ti and its alloys are well-known to be resistant to oxidation at low temperatures owing to the formation of a dense natural oxide layer on the surface [1]. However, the performance of Ti alloys at high temperatures is limited owing to the reduction in the oxidation resistance and subsequent degradation of the alloy. Applications of Ti alloys are often limited at temperatures above 550°C, e.g., in the case of Ti-6Al-4V alloy [2] at temperatures greater than 400°C, owing to the growth of the oxide layer above these temperatures and the conversion of the oxide to non-protective state [3]. Alloying with Si is considered as a favorable approach to improve the oxidation resistance and high temperature creep behavior of Ti. Ti_5Si_3 in the Ti-rich side of Ti-Si binary system is an attractive silicide compound owing to its high melting point (2130°C), low density (4.3g/cm^3), and its ability to keep high strength up to and beyond 1200°C [3]. Si dissolved into the oxide layer reduces the oxygen diffusion rate through this layer and improves stress alleviation, thus leading to the formation of an increasingly compact and less porous oxide scale [4]. Zr is also a well-known alloying element for improving the properties of Ti alloys at high temperatures by increasing the matrix hardenability and through microstructural modification [5]. However, the oxidation behavior in simultaneous addition of Si and Zr in Ti needs to be studied further, particularly at temperatures related to the operation. Moreover, an extensive understanding about the relationship between the formation of the oxide scale and oxidation resistance is necessary. This study aims to investigate combined effect of Zr and Si on isothermal oxidation of Ti at 820°C, which is the operating temperature of exhaust valves.

2. Experimental

Three alloy samples with a fixed Zr content of 5mass% and two different Si contents (5mass% and 10mass%) were prepared from pure Ti, Si and Zr in the form of button ingots (weight ~20 g) via argon arc melting. To ensure sufficient compositional homogeneity of the alloys, each ingot was melted three times. For oxidation test, samples with dimensions of 15×10×2 mm were machined from the ingots and ground with SiC papers with grit sizes ranging from 120 to 800. Each sample was placed in an alumina crucible before isothermal oxidation. Isothermal oxidation was performed under an ambient atmosphere in the furnace at the operating temperature of exhaust valves (820°C), for two different durations (25 and 50 h). After the grinding, the samples were weighed before and after the oxidation test using an analytical balance with a precision of ±0.0001 g. Following the oxidation exposure, all the specimens were air-cooled to room temperature. After air-cooling, the specimens were reweighed. The as-cast microstructure was evaluated using scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector. Phase analysis of samples oxidized for 50 h was performed by means of a Smartlab diffractometer (Rigaku, Japan), operated at a current of 200 mA and a voltage of 45 kV. The angle step size was of 0.01° and the scanning speed was of 1.5°/min. Phase diagrams plotted for oxygen partial pressure were calculated by Factsage 7.1 to predict the formation of oxide layer and phase equilibrium of the Ti-Si-Zr ternary system.

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3. Results and discussion

Fig. 1 displays back-scattered electrons (BSE) images of as-cast microstructure of Ti-5mass%Zr-10mass%Si alloy. This image indicates that the as-cast microstructure of Ti-5mass%Zr-10mass%Si alloy is composed of α-Ti matrix and an intermetallic compound. As a result of EDS as shown in Table 1, the α-Ti matrix marked as 1 contains a large amount of Si that can be caused by a high cooling rate. Area 2 corresponds to Ti_5Si_3 formed by a eutectic reaction. Zr is fully dissolved into both the α-Ti matrix and the Ti_5Si_3. Zr would substitute some of the Ti and form $(Ti,Zr)_5Si_3$. Therefore, Ti-5mass%Zr alloy might only comprise a solid solution because Zr is entirely soluble in Ti [6]. The as-cast microstructure of Ti-5mass%Zr-5mass%Si alloy would have a small amount of Ti_5Si_3.

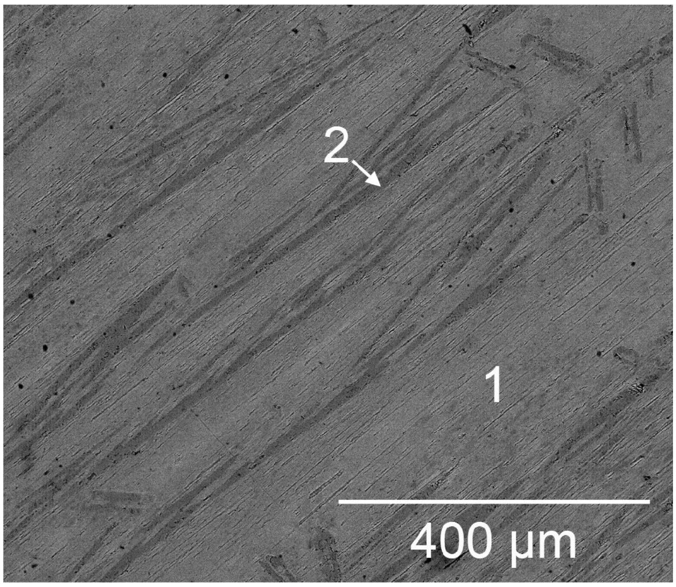

Fig. 1. SEM-back-scattered electrons (BSE) images of the as-cast microstructure of Ti-5mass%Zr-10mass%Si alloy

TABLE 1

Analyzed composition of each area in the as-cast microstructure of Fig. 1

Area	Composition (mass%)		
	Ti	Zr	Si
1	81.83	06.21	11.96
2	67.18	06.86	25.96

The results from the weight change measurements presented in Fig. 2 show a weight increase for all specimens. This weight gain would be attributed to both the oxygen associated with the oxide on the surface and the dissolved oxygen in the Ti samples. Based on the weight measurements, the following assumptions can be made: (i) the addition of Zr and Si into Ti decreases weight gain down, (ii) the difference in weight gain at the experimental temperature for the two holding times is more significant in the sample in which only Zr was added than those in which Zr and Si were simultaneously added, and (iii) only the 5mass%Zr-added alloy shows an increasingly retarded weight gain than that of Ti-6Al-4V, which was reported in a previous report [7]. The significant decrease in the oxidation for Si-added alloys compared with only Zr-added alloy would be obviously owing to SiO_2 formation on the surface.

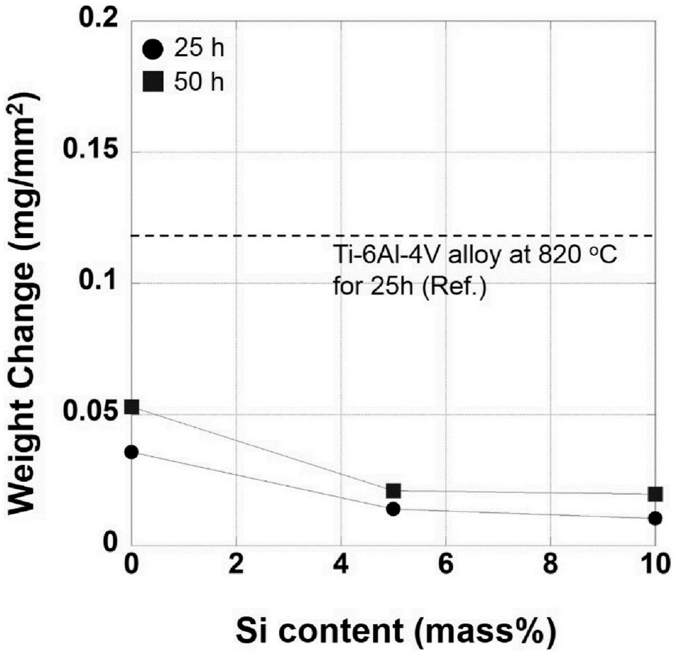

Fig. 2. Results from the weight change measurements with reference data [7]

XRD results of samples after the oxidation at 820°C for 50 h are given in Fig. 3. The oxidized layer of the Ti-5mass%Zr alloy comprises rutile TiO_2 and ZrO_2. The α-Ti peaks were also detected owing to the penetration of X-rays under the oxide layer through the alloy. However, the XRD pattern of the Ti-5mass%Zr-10mass%Si alloy sample revealed the presence of rutile TiO_2, ZrO_2, and SiO_2 as oxide layer. The α-Ti and Ti_5Si_3

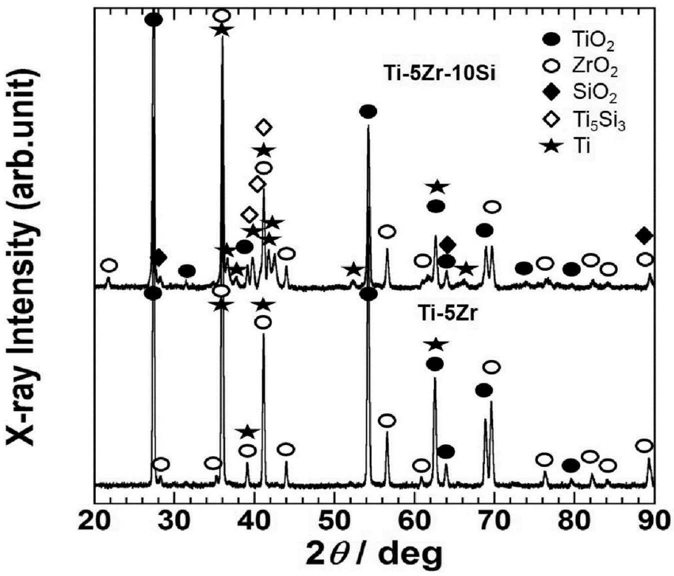

Fig. 3. XRD results of samples after the oxidation at 820°C for 50 h

were also detected from the oxidized Ti-5mass%Zr-10mass%Si alloy samples. Temperature versus Si mass fraction of Ti-Si-Zr ternary phase diagram with a fixed Zr content (5mass%) calculated by Factsage 7.1 are shown in Fig. 4. At the experimental temperature, even with a small amount of Si under 1mass%, the alloys contain Ti_5Si_3 that forms SiO_2 during the oxidation. Therefore, Ti-5mass%Zr-5mass%Si alloy would also have a SiO_2 layer on the oxidized surface, which can result in an oxidation resistance that is similar to that of 10mass%Si added alloy reasonable.

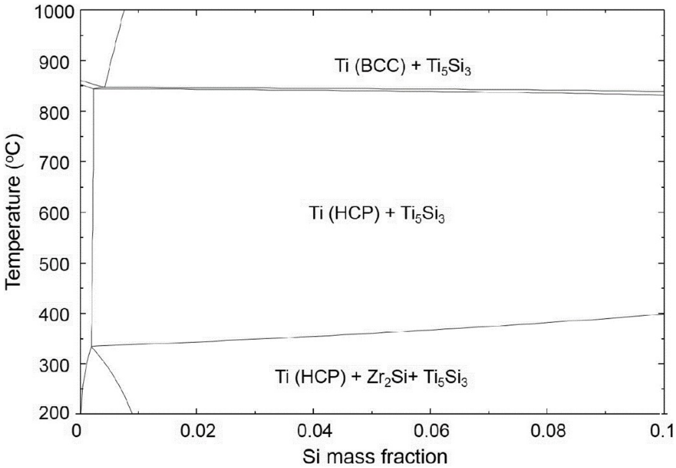

Fig. 4. Vertical section plotted for temperature versus Si mass fraction of Ti-Si-Zr ternary phase diagram with a fixed Zr content (5mass%) calculated by Factsage 7.1

Phase diagrams plotted for oxygen partial pressure versus Si mass fraction with a fixed Zr content (5mass%) and temperature (820°C) in Ti-Zr-Si system calculated by Factsage 7.1 are shown in Fig. 5. Oxide formation with lower oxygen partial pressure is generally understood to be preferential. Fig. 5 indicates the formation of ZrO_2 as the primary oxide throughout the entire Si content range. Following the primary oxide formation, oxidation proceeds with the appearance of Ti_3O_5 and the subsequent appearance of TiO_2. In the case of Si addition, SiO_2 is additionally formed. Therefore, the joining of the SiO_2 would result in the formation of a compact oxide layer and decrease inward diffusion of oxygen. According to previous studies [8,9], the reduction in oxidation rates with increasing Si concentration is primarily associated with the appearance of Ti_5Si_3, which is the main source of SiO_2 formation. Si dissolves in the oxide scale during oxidation and consequently decreases oxygen diffusion in the TiO_2 layer. Addition of only Zr also decreased the oxidation rate of the Ti substrate. Zr addition reduces the Si solubility in α-Ti, thus leading to increased precipitation of Ti_5Si_3, which implies that an appropriate combination of Si and Zr in Ti should result in simultaneous improvement of oxidation resistance and high temperature strength.

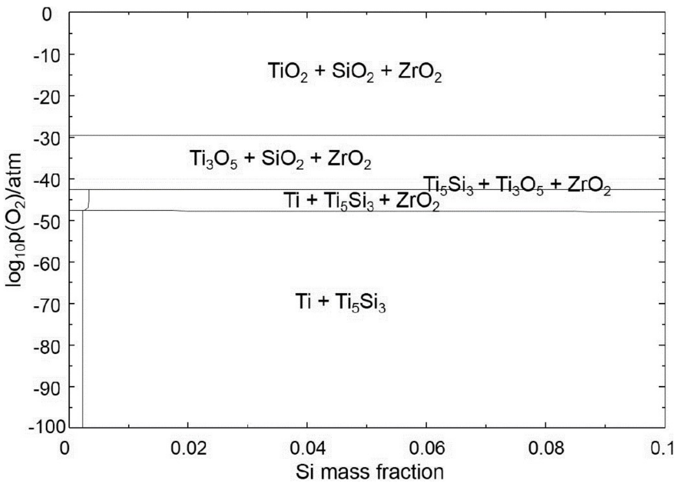

Fig. 5. Phase diagrams plotted for oxygen partial pressure versus Si mass fraction with a fixed Zr content (5mass%) and temperature (820°C) in Ti-Zr-Si system calculated by Factsage 7.1

4. Conclusions

Simultaneous addition of Si and Zr into Ti resulted in the distribution of fully Zr soluble α-Ti and Ti_5Si_3 phase in the matrix. Only the addition of 5mass%Zr can significantly retard the oxidation rate, while the simultaneous addition of Zr and Si resulted in a greater increase in the oxidation resistance. The oxide layer formed after addition of Zr and Si comprised TiO_2, ZrO_2, and SiO_2. Significant increase in oxidation resistance is mainly attributed to the joining of SiO_2. Zr addition can be used as an approach to preserve high temperature mechanical property and oxidation resistance since Zr dissolution in α-Ti decreases Si solubility and leads to the increased precipitation of Ti_5Si_3.

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