Alloying Effects and Temperature Dependency of Oxidation Behavior in Near-α Titanium Alloys.

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論 文 名　：Alloying Effects and Temperature Dependency of Oxidation Behavior in Near-α Titanium Alloys.

(ニアαチタン合金の酸化挙動に及ぼす合金添加の影響と温度依存性)

区　　分　：甲

論 文 内 容 の 要 旨

Thesis Summary

The main objective of this study was the investigation of the effects of elements (Ga, Sn) and microstructures on oxidation behaviors of near-α Ti alloys at elevated temperatures (650-750 °C) after long exposure time (up to 500 h) in ambient air.

It has been shown that alloying elements, temperature, time and microstructures affect oxidation behaviors. Some additional alloying elements decrease oxygen vacancies in TiO_2 thus decreasing the overall oxidation rate through valence control rule, some elements can form a discrete layer working as a barrier to prevent oxygen diffusion, and some elements affect the adherence of the oxide layer to the metal substrate. For conventional Ti alloys, a logarithmic law has been obtained at low temperature, and changed to parabolic and linear law or mixed rate law with increasing temperature and time. The change of oxidation kinetics were combined with the change in oxide formation and oxygen diffusion, such as the porosity of oxide scale, the composition of oxides, temperature dependency of oxygen diffusivity etc. In addition, microstructures, like bimodal and lamellar microstructures, also affect oxidation process especially on oxygen diffusion process.

To investigate the effects of alloying elements on oxidation behavior, a Ga-containing and a Sn-containing near-α Ti alloys were studied. The microstructures' effects were also considered. It was shown that the replacement of Sn with Ga decreased the weight gain of the oxidation sample during oxidation, suppressed oxide growth, and improved adherence between the oxide and substrate. In Ga-containing alloy, there was no Ga segregation at the oxide/substrate interface, and the formation of $(Al, Ga)_2O_3$ and $(Ga, Al)_2TiO_5$ was suggested. Unlike conventional Ti alloys, recrystallization occurred near the oxide/substrate interface, which may contribute to the release of stress, improvement of the

adherence between the oxide and substrate, and prevention of the spallation of oxides. In both alloys, lamellar structures showed a smaller weight gain compared to the bimodal structures.

As the Ga-containing alloy showed better oxidation resistance compared to that of Sn-containing alloy and recrystallization was observed near the oxide/substrate interface, the effects of temperature and time on the oxidation behaviour (especially on oxidation reaction rate and α-case formation) of the Ga-containing near-α Ti alloy and the temperature dependence of its recrystallization process were examined. It was shown that oxidation follows a parabolic relationship at 650 °C and a parabolic-cubic relationship at 700 °C and 750 °C with the abundance of Al_2O_3 in oxide layers. The amount of Al_2O_3 increased with temperature after the dissolution of Ga_2O_3 species in the Al_2O_3 phase. The activation energy of α-case formation was close to the magnitudes obtained for conventional titanium alloys despite its temperature-dependent recrystallization observed near the oxide/metal interface at 700 °C and 750 °C. Recrystallization also occurred in the substrate at the oxide/metal interface in Ti-4Al and Ti-8Al system. N showed higher concentration at the oxide/metal interface in Ti-4Al, Ti-8Al, and Ga-containing alloy except for Sn-containing alloy. Based on the element analysis and the phase diagram of Ti-Al-N system, the formation of grains with Ti_3AlN and Ti_2N were suggested at the interface due to the high concentration of N. Fine recrystallized grains were observed near the interface due to lattice misfit strain.

In summary, this dissertation investigates the oxidation behaviors of a Sn-containing Ti alloy and a Ga-containing Ti alloy. The mechanism on the effects of alloying elements, temperature and time on oxidation behaviors was studied.