

論文 / 著書情報  
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Title(English)	Hydrogen Permeability in the Scales of Iron Oxide at 973 K under Constant Oxygen Activity
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(博士課程)  
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## 論文要旨

THESIS SUMMARY

専攻 : Department of	Metallurgy and Ceramics Science	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 Doctor of	(Engineering)
学籍番号 : Student ID Number			指導教員 (主) : Academic Advisor(main)	Prof. Toshio Maruyama	
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words )

The title of the thesis is "Hydrogen Permeability in the Scales of Iron Oxide at 973 K under Constant Oxygen Activity". The thesis is divided into five chapters,

**Chapter 1: "Introduction"**. Ferritic and Austenitic heat resistant steels are currently used as tubing materials of superheaters and reheaters in advanced power plants. The steam oxidation behavior of these steels remains a major issue. Protective chromium oxide ( $\text{Cr}_2\text{O}_3$ ) that is expected to be formed on the surface of the tube was retarded by the enhanced growth of non-protected iron-oxides as the outer scale and Fe-Cr spinel as the inner scale. This oxidation behavior was not only observed in the steam side, but it also observed in the air side. It is strongly suggested that hydrogen permeation from the steam side to the air side of boiler tube played important role. Hydrogen permeability measurement is one of the effective ways to understand this mechanism. The objective of this thesis is to clarify the hydrogen permeation through iron-oxides under constant oxygen activity at 973 K, which is the target temperature of Advanced USC power plants. The information of hydrogen permeability constant of iron-oxide will provide valuable information to determine the significance role of iron oxide layer in the permeation of hydrogen from the inner side to the outer side of the boiler tube.

**Chapter 2: "Phase stability of iron oxides in the Pd-Fe-O system by electro-motive force measurement"**. The iron oxide for the hydrogen permeability measurement is required of a single phase with a known thickness. There are three phases of iron oxides, wüstite ( $\text{Fe}_{1-x}\text{O}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ). Accurate phase boundary between Fe oxide and Pd-Fe alloy is required to determine the alloy composition and the oxidation condition to obtain desired Fe oxide on the alloy. In this study, thermodynamic stability of iron oxides in Pd-Fe-O system was determined from the Pd-Fe alloys in the range composition of 1-at% Fe to 64-at% Fe at the temperature 973 K to 1073 K. The equilibrium oxygen partial pressure of Pd-Fe alloy/iron-oxide was measured with oxygen concentration cell made by solid electrolyte of Ca-stabilized  $\text{ZrO}_2$ . Based on the obtained result, the phase boundary of iron-oxides with Pd-Fe alloy was determined, and the thickness of iron-oxide was estimated as a function of equilibrium oxygen partial pressure and alloy compositions.

**Chapter 3: "Formation of iron oxides on Pd-Fe alloy by high temperature oxidation"**. Single-phase of iron oxide is grown directly from the Pd-Fe alloy by high temperature oxidation. The oxidation condition was determined from the phase boundary between Fe oxide and Pd-Fe alloy in the Chapter 2. Oxygen partial pressure was controlled by supplying gas mixture of Ar- $\text{H}_2$ - $\text{H}_2\text{O}$  with a certain  $\text{H}_2/\text{H}_2\text{O}$  ratio. Oxidation at 1073 K for 259.2 ks has shown that single-phase wüstite formed on the alloy. Nevertheless, alloy composition and thickness of the oxide have indicated that the oxidation rate at this temperature was still too low to reach equilibrium condition. Furthermore, oxidation at 1273 K until 518.2 ks were conducted and it successfully formed single-phase of wüstite and magnetite on Pd-Fe alloy. Oxide precipitate also formed in the alloy substrate. The total thicknesses of the oxide, which corresponds to the thickness of outer oxide scale and oxide precipitate, were close to the estimated values. The composition of the alloy also shows that equilibrium condition has been reached at this temperature. However, the compositions were slightly smaller than that the expected value, which may come from the less accuracy of the estimated  $P_{\text{O}_2}$  at this temperature. The results above oxidation experiments have clarified that the phase boundary diagram between Fe oxide and Pd-Fe alloy, which developed in the Chapter 2 was applicable to form single-phase iron oxide with the expected thickness.

**Chapter 4: "Hydrogen Flux Permeated Through Iron Oxide at 973 K under Constant Oxygen Activity"**. Hydrogen permeation measurements through single-phase of magnetite and wüstite

have been conducted at 973 K under constant oxygen activity. Pd-Fe alloy was sandwiched into two compartments of hydrogen provided side and detected side. The oxygen activity of both compartments was kept at the same value by supplying gas mixture of Ar-H<sub>2</sub>-H<sub>2</sub>O in the hydrogen provided side and Ar-CO-CO<sub>2</sub> in the detected side with certain H<sub>2</sub>/H<sub>2</sub>O and CO/CO<sub>2</sub> ratios. The alloy was first oxidized at 1273 K to form wüstite or magnetite layer with the certain thickness. The temperature then decreased to 973 K for the permeation measurement. The oxygen activity at 973 K was carefully maintained at certain value so that it formed the same oxide thickness as the oxidation at 1273 K. The hydrogen permeability of magnetite and wüstite from the measurement were  $8.1 \times 10^{-11} \text{ molH m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$  and  $5.1 \times 10^{-11} \text{ molH m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$ . Those values are about one order of magnitude lower than that the reported hydrogen permeability constant of iron. This result may indicate that the permeation of hydrogen through boiler tube with the co-existence of magnetite or wüstite scale will be determined by the hydrogen permeation of the boiler material rather than the iron oxide itself. This is due to the condition that the thickness of boiler material will be more than one order of magnitude thicker than the thickness of the oxide scale.

**Chapter 5: "Conclusion".** The hydrogen permeability of single-phase wüstite and magnetite at 973 K in a steady-state condition has been determined. The result clarified that the hydrogen permeability of iron-oxide does not play important role in the growth of iron-oxide in the outer side of boiler tube.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 2 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 2 copies of 800 Words (English).