

氏 名 渡邊 崇

学位（専攻分野） 博士（学術）

学位記番号 総研大甲第 1485 号

学位授与の日付 平成 24 年 3 月 23 日

学位授与の要件 物理科学研究科 核融合科学専攻
学位規則第 6 条第 1 項該当

学位論文題目 Studies on electrochemical surface modification for
molten salt blanket system in fusion reactor

論文審査委員 主 査 教授 佐藤 元泰
教授 相良 明男
教授 室賀 健夫
教授 深田 智 九州大学
准教授 鈴木 晶大 東京大学

論文内容の要旨

This doctoral dissertation presents studies for materials for devices in molten fluoride salt blanket system in fusion reactor. When steel materials are employed as a structural material, a critical issue is its corrosion by the fluoride salts. To prevent it, many kinds of ceramics and coating processes have been discussed about compatibility with fluoride salts. However, there are many problems: large area coating over 1000m², toughness against peeling and crack of the coating, waste product after the coating process and healing for damage parts. In this dissertation, a surface modification method through an electrochemical process using molten fluoride salt itself was proposed to form a robust functionally graded compositional nitride layer at the structural material surface for overcoming the above problems.

First, several kinds of oxides and nitrides were thermodynamically considered about compatibility with fluoride molten salts. The thermodynamic consideration predicted that oxides dissolve into molten fluoride salts while nitrides have compatibility with molten fluoride salt. And prior to development of the surface modification process, compatibilities of oxides and nitrides in FLiNaK at 600°C were examined in immersion test over 1000 hours using Er₂O₃, Y₂O₃, Al₂O₃ and AlN bulk test specimens. The results demonstrated excellent compatibility of nitride AlN with molten fluoride salt FLiNaK. Secondly, coating processes were considered. To form a robust graded compositional nitride layer using compositional elements from the structural material, an electrochemical process was proposed. In the process, the surface of structural material is electrochemically treated in molten fluoride salt which contains Li₃N as a nitrogen source. Thirdly, for the experiments which employ molten fluoride salts needing dry environment at high temperature over 500°C, an original experimental setup was assembled in a dry Ar gas filled glove box. It consists of a stainless steel reactor, a nickel crucible, thermocouples, heaters and electrodes. The electrochemical measurement and nitriding of 316 stainless steel (ss316) surface in a binary eutectic mixture of LiF-KF (FLiK) including Li₃N over 500°C were conducted using it. Aluminum rods were used as counter and reference electrodes. The potential standard was determined by the following equilibrium redox reaction of aluminum lithium alloy: $\text{Al} + \text{Li}^+ + e^- = \text{LiAl}$. The specimen of ss316 was bound tightly by a nickel wire at an end of nickel rod and it worked as working electrode. On the basis of the measurement of cyclic voltammogram of ss316, the nitriding condition was decided. Fifthly, the ss316 surface was nitrated on a potentiostatic condition of 1.0V with respect to lithium redox potential as a standard potential, ie, 1.0V vs. Li/Li⁺ at 600°C. The specimens were analyzed using analytical methods, such as electron probe micro analyzer (EPMA), X-ray diffraction (XRD), electron energy dispersive X-ray spectrometry (EDX), X-ray photoelectron spectroscopy (XPS), and scanning electromicroscopy (SEM). According to EPMA measurement, for 100 minute treatment,

nitrogen was introduced into a depth of 35 μm from the surface and, for 240 minute treatment, nitrogen was done into a depth of 65 μm . Then, it was revealed that chromium nitride CrN was formed as a nitride. XRD and EDX measurements demonstrated that the initial face-center cubic (fcc) structure transformed to a body-centered tetragonal (bct) structure by the nitriding without changing metal ratios. Formation of solid solution $\alpha\text{-Fe}_{n(n>8)}\text{N}$ was also suggested. Although oxygen impurities have also been expected to be introduced to the nitride layer, oxygen was not introduced into the layer. This means that only nitrogen was mainly introduced in the layer through the treatment. Finally, considering the experimental conditions such as temperature, nitrogen concentration and specimen composition, nitride formation was theoretically discussed based on combination of thermodynamics and electrochemistry. CrN, Cr₂N, Fe₂N and Fe₄N were considered from composition of ss316. Potential-nitride formation diagram and potential-nitrogen ion concentration diagram were made. From discussions on formation of these nitrides based on these conditions, it was theoretically derived that CrN is most stable. This theoretical consideration was well in agreement with the experimental result. In conclusion, these results demonstrate availability of this nitriding method and give a guideline for optimization of this nitriding process in molten fluoride salts.

This doctoral dissertation consists of five chapters and one appendix. Chapter 1 presents back ground and proposal of this work, ie, issues and problems on a molten salt blanket system in a fusion reactor. Chapter 2 presents thermodynamical discussion of compatibilities of several ceramics (metal oxides and nitrides). Compatibilities for those ceramics were evaluated based on thermodynamical theory. The prediction indicated that nitrides are compatible with molten fluoride salts. Chapter 3 presents the experimental descriptions and results. Introduction of nitrogen into SS316 specimen surface and formation of nitride layer were described. Chapter 4 presents theoretical explanation based on thermodynamics and electrochemistry. Formation of nitrides about iron and chromium is discussed. Chapter 5 presents conclusions. Appendix presents the results of immersion test for 4 bulk specimens of Er₂O₃, Y₂O₃, Al₂O₃ and AlN in molten FLiNaK at 600°C over 1000 hours.

In recent years, nitrides have been focused on as fluorescent materials and magnetic materials. Especially, iron nitride, $\alpha\text{-Fe}_{n(n>8)}\text{N}$, has expected as a alternative material of Nd, rare-earth element. Nitriding technique established in this work will be able to be applied not only to blanket system in fusion reactor, but also to many kinds of industrial applications.

核融合炉液体ブランケットの有力候補である弗化物溶融塩(FLiBe 等)を用いたシステムでは鉄鋼系金属材料が構造材料の第一候補である。しかし、腐食対策が重要課題の一つである。セラミクス被覆による腐食対策が従来検討されてきたが、弗化物塩との共存性、大面積かつ複雑形状の被覆、被覆処理後の廃棄物処理、被覆層の堅牢性、修復方法の確立等が課題である。本論文出願者はこれらの課題を克服すべく世界に先駆けて弗化物溶融塩そのものを用いた電気化学的手法による金属材料表面改質法を提案した。独自に考案した実験装置によりステンレス鋼表面に数 10 μm 以上に及ぶ窒化物傾斜機能層形成に成功した。

当該論文では、先ず第 1 に熱力学的解析により被覆候補材料として窒化物が有望であることを見出すと共に、各種セラミクスの焼結試験片を 600 $^{\circ}\text{C}$ の溶融塩 FLiNaK に浸漬する予備実験により、窒化物が弗化物溶融塩との優れた共存性を示すことを確認した。第 2 にステンレス鋼表面の窒化処理法として、従来の熱化学的手法によるセラミクス被覆とは異なり、 Li_3N を添加した弗化物溶融塩中で電気的駆動力により窒化物傾斜機能層を形成する電気化学的な方法を提案した。第 3 に弗化物溶融塩のための実験装置を開発した。Ar ガス置換したグローブボックス内に弗化物溶融塩を入れた密閉容器と電気ヒーターからなる電気化学実験装置を構築した。第 4 にそれを用いて溶融塩 FLiK 中の 316 ステンレス鋼の電気化学基礎データであるサイクリックボルタモグラムの測定し、 Li_3N 添加系と未添加系の比較に基づき窒化処理の際の電位を決定した。第 5 に Li の酸化還元電位を基準として +1.0V の定電位条件で、SUS316 鋼試料表面を処理した。X 線回折、電子線プローブマイクロアナライザ、X 線光電子分光、走査型電子顕微鏡、エネルギー分散型 X 線分析の各種分析手法により窒化物層を詳細に調べた。100 分間及び 240 分間の処理により各々 35 μm 及び 65 μm の厚さの窒素導入層が形成され、主な窒化物として CrN の形成に加え、fcc 構造から bcc 構造への変態と共に $\alpha\text{-Fe}_{100-x}\text{N}_x$ 固溶体層形成も示唆された。第 6 に温度、弗化物溶融塩中窒素イオン濃度、基材組成、電極電位等の相関関係について、電気化学と熱力学に基づき理論解析を行った。窒素と金属間の反応について Nernst の式による窒化物生成電位の理論式を示し、温度、溶融弗化物塩中窒素イオン濃度、電極電位の条件と窒化物生成挙動の関係を示すダイアグラムを作成し、 Fe_2N 、 Fe_4N 、CrN、 Cr_2N 間の反応を考察した。これらの解析結果は Fe と Cr を含む系の窒化物生成挙動についての実験結果を良く説明した。さらに、既存データベースでは未整備の弗化物溶融塩中の Fe の反応に関わる標準電極電位を窒化物生成電位の計算過程から得た。以上の実験と理論的解析の結果は処理条件最適化のための指針を与えると共に、この手法の有効性を実証する。また、弗化物溶融塩中での窒化処理はその場修復の可能性も開拓する。さらに、窒素を導入した Fe は Nd の代替材料として強磁性材料創成への産業応用へ可能性も示唆する。

電気化学的研究手法による弗化物溶融塩に関わる物質研究は今後の核融合科学に関わる材料研究の可能性を切り拓き、その独創性、新規性および発展性は高い評価に値し、核融合炉の実現に向けて大きく貢献するものと期待される。よって、本審査委員会は本論文が博士の学位論文として十分価値があり、合格であると判定した。