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学位論文題目 Development of Er_2O_3 Coating by MOD Method for
Liquid Blankets

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In the magnetic confinement fusion reactors, blanket is one of the most important components and has the following main functions: heat generation and extraction, tritium breeding, and radiation shielding for superconductor coils. Compared with the solid breeder blankets, liquid breeder blankets are more attractive for the future DEMO reactors because of their high operation temperature, simple structure, no irradiation damage on the breeding material and no decrease in the tritium breeding capability with operation time, and so on. As the liquid breeders, liquid metal (Li, Li-Pb) and molten salt (Flibe: $2\text{LiF}+\text{BeF}_2$) have widely been examined. However, there are some critical issues in these liquid blankets, e.g. magneto-hydrodynamics (MHD) pressure drop in the case of liquid metal blankets and tritium permeation through the structure materials of blanket in the case of molten salt and Pb-Li blankets. To solve these issues, fabrication of ceramic coating on the surface of the metal ducts has been proposed.

The candidate materials of ceramic coating need to have high tritium permeation reduction factor for application to tritium permeation reduction, and high electrical resistivity for application to MHD pressure drop mitigation, respectively. The coating materials also need to have good compatibility with the liquid breeders if the coating is to be made on the interior surfaces. Among the ceramic coating materials investigated, Er_2O_3 coating has been considered as a promising candidate material for the coatings in those liquid blanket systems because it showed superior compatibility with liquid Li of up to 700°C , high electrical resistivity and good deuterium permeation barrier performance when the coating was fabricated on the Reduced Activation Ferritic/Martensitic (RAFMs) steels by radio frequency sputtering and filtered arc plasma deposition methods. However, these methods cannot be used to fabricate the coating on the surface of complex shapes, especially on inner surface of long ducts.

The metal organic decomposition (MOD) by dip-coating method is one of the potential methods for the fabrication of coating on the complex surface, especially the pipe interiors. This method proceeds with repeated dipping into the precursor, withdrawal and drying, followed by baking. The purposes of the present study are: (1) to investigate and optimize the fabrication process of MOD Er_2O_3 coating with dip-coating method; (2) to examine the performance of MOD coating with respect to applications to liquid blankets; (3) to clarify the means to improve the performance of the coating according to the microstructural and microchemical characterization of the coating and the substrate.

In this study, the materials used as the substrate are two kinds of ferritic steels: Fe-18Cr based commercial ferritic steel (SUS430) and Fe-9Cr-2W-0.1C based candidate Reduced Activation Ferritic/Martensitic steel (RAFMs steel: JLF-1). Since the main difference in the composition of the two steels is the chromium level, the impact of the chromium level can be investigated by comparing the performances of coatings on the two substrates. MOD precursor layers, which were mainly composed of erbium carboxylate, were formed by dip-coating method and then decomposed into the Er_2O_3 coating by baking in an environment containing oxygen to remove the carbon of organic. Microstructure of the coating and composition of the substrate including oxidized layer were examined by SEM/EDX (Scanning Electron Microscope/Energy Dispersive X-ray Spectrometer), XPS (X-ray Photoelectron Spectroscopy) and XRD (X-Ray Diffraction). The performances of the coating for the applications to liquid blankets were examined by electrical resistivity measurements, compatibility tests with Li and hydrogen isotope permeation tests.

With different speeds of withdrawal from the precursor slurry, coated specimens were fabricated with the repeated dipping for 20 times followed by baking. The coating thickness was proportional to the repetition time of the dipping and to the $2/3$ power of the withdrawal speed, which is consistent with a model evaluation considering gravity, viscosity and surface tension of the precursor slurry.

When Er_2O_3 coatings on SUS430 substrate were baked in air, erbium organic completely

decomposed above 450°C and formed the Er₂O₃ coating with cubic phase according to the XRD analysis of coating. When baked at 600°C for better crystallinity in air, thin oxidized layer (<0.1 μm) with main composition of Cr₂O₃ was formed below the coating. At room temperature, the coating with thickness of 0.5 μm had high electrical resistivity up to 10¹¹ Ωm which satisfied the design requirement of liquid Li blankets (10⁴ Ωm). The coating survived after the static Li exposure test for 280h at 500°C, which means that it has good compatibility with Li. Compared with the bare SUS430 substrate, coated specimen has a deuterium permeation reduction factor of about 50 at 600°C.

When Er₂O₃ coating on JLF-1 substrate was baked at 600°C in air, the coating almost peeled off from the substrate after static Li exposure test for 5h at 500°C and had hydrogen permeation reduction factor of only 15 at 600°C. From the elemental depth profile of the coating with XPS analysis, thick Fe₂O₃ layer was formed on JLF-1 substrate. Coating surface on JLF-1 substrate was very rough compared with that on SUS430 substrate. The reason of the inferior performances of the coating on JLF-1, relative to that on SUS430 seems to be attributed to the Fe₂O₃ layer, which has a very different coefficient of thermal expansion from that of Er₂O₃ compared with Cr₂O₃ and, thus could introduce small cracks in the coating during the cooling down after the baking. Because JLF-1 has low chromium level and high oxidization potential in air compared with high chromium level of SUS430, decrease of oxygen partial pressure in the baking atmosphere is considered to be a possible way to suppress the formation of Fe₂O₃ layer in the oxidized layer of JLF-1 surface.

To suppress the formation of Fe₂O₃ layer and remove the carbon of organic, coating on JLF-1 substrate was baked at 700°C for 1h in commercially pure Ar where oxygen impurity was ~10ppm during the baking process in the furnace. XPS analysis showed that erbium organic was completely decomposed into Er₂O₃ without the remaining carbon and a Cr₂O₃ layer was formed in the oxidized layer. In this case, the coating had a smooth surface without the cracks compared with those baked in air while some bulgy parts including carbides or carbon were found. After the static Li exposure test for 5h at 500°C, the coating still covered 70% area of the specimen. Though the stability of coating was improved, further improvement is necessary to reduce the bulgy parts of carbon or carbides whose dissolution into Li lead to the exfoliation of coating. Hydrogen permeation reduction factor of the coating was increased from 15 to ~100 at 600°C by changing the baking atmosphere from air to Ar.

The coatings on JLF-1 and SUS430 were also fabricated by baking at different temperatures in baking atmospheres with different oxygen partial pressures. The results showed that high baking temperature and low oxygen partial pressure were effective to form Cr₂O₃ layer on JLF-1 substrate. A model could qualitatively explain the formation condition of Cr₂O₃ which was affected by the baking temperature, oxygen partial pressure and chromium level of substrate. The formation of Cr₂O₃ layer depends on the balance between the diffusion flux of chromium cations from the substrate and the supply of the oxygen anions which diffused through the coating layer from the baking atmosphere. The low oxygen pressure would suppress the formation of Fe₂O₃ by decreasing the diffusion flux of oxygen anions through the coating layer and the high temperature would enhance the diffusion of chromium cations to the substrate surface inducing formation of the Cr₂O₃ layer on JLF-1.

In summary, dip-coating by MOD method is suitable for the coating of Er₂O₃ on large area and complex surfaces because it is a simple process and is controllable of thickness. The coating with thickness of 0.5 μm had high electrical resistivity and almost satisfied the design requirement of liquid Li blankets. In the case of high Cr steel substrate of SUS430, baking in air induced formation of Cr₂O₃ layer on the substrate, which kept the good coating performances with respect to surface smoothness, compatibility with Li and hydrogen permeation reduction. However, in the case of low Cr steel substrate of JLF-1, the baking in air induced thick Fe₂O₃ layer, resulting in much inferior coating properties. Very different coefficient of thermal expansion of Fe₂O₃ from that of Er₂O₃, which could lead to micro cracking of the coating by the temperature change, is considered to be responsible. By decreasing the oxygen partial pressure in

the baking atmosphere and increasing baking temperature, Cr_2O_3 layer was formed instead of thick Fe_2O_3 layer on JLF-1 substrate surface and then the coating performances were improved significantly.

Thus it is critically important to avoid the formation of Fe_2O_3 layer by controlling the oxygen partial pressure of the baking atmosphere. By systematic tests with different baking temperatures and oxygen partial pressures, the conditions to avoid the formation of Fe_2O_3 layer were indicated for the two steels, and possible mechanisms of the effects of these parameters were identified by a model considering diffusion of oxygen anions and chromium cations in the coating and the substrate, respectively. However, the control of baking atmosphere would not be sufficient for the coating on JLF-1 to have high compatibility with liquid Li. Enrichment of Cr in the surface of the substrate or use of high Cr level RAFM substrate could be possible ways for further improvements.

核融合炉の炉心を取り囲むように配置されるブランケットは、炉心で発生した中性子のエネルギーを熱に変え取り出すとともに、リチウムとの核反応により燃料トリチウムを生成し取り出す重要な機器である。高性能ブランケット概念として液体リチウム、熔融塩などの高温融体の液体増殖材をブランケット内に循環させる「液体増殖ブランケット」が検討されているが、液体リチウムブランケットでは磁場中での高速流動に伴って配管内に発生するMHD圧力損失が、熔融塩ブランケットでは配管外へのトリチウムの透過漏えいが、それぞれ対応すべき重要課題である。これらを低減する手段として配管へのセラミックス被覆が検討されている。

これまでの研究により、電気絶縁性が高く、液体リチウムとの共存性に優れ、水素透過低減効果も大きい酸化エルビウムが液体リチウム、熔融塩両方のブランケットで有力な被覆候補材と見なされている。しかしこれまでの研究の多くは、実験室での原理実証のため行われてきた物理蒸着被覆によるものであり、これらの方法によりブランケットの複雑形状表面の被覆を行うことは困難である。Zhang氏は、長尺の配管内面にも被覆可能で実用性に優れた「浸漬被覆法」に着目し、金属錯体分解(MOD)による酸化エルビウム被覆を初めて試みた。被覆法の最適化を進めるとともに、浸漬後の引き上げ速度効果などを詳細に調べモデル評価と合わせることで、被覆厚さの制御が高い精度で可能であることを示した。基板材には、ブランケット候補材である低放射化フェライト鋼JLF-1(9%Cr)に加え、Cr濃度効果を比較検証するため工業フェライト鋼SUS430(18%Cr)を用いた。浸漬後の酸化熱処理条件の最適化を行い、大気中熱処理でSUS430基板上に作製した被覆が優れたリチウム耐食性と水素透過低減効果があることを確認した。しかし、JLF-1基板では、リチウム耐食性、水素透過低減効果ともにSUS430基板に比べて劣る結果となった。Zhang氏は詳細な分析により、MODの酸化熱処理によりSUS430基板上には酸化クロム層が中間層として形成するが、Cr濃度が低いJLF-1では酸化鉄層が中間層として形成し、酸化クロムに比べて酸化鉄の大きな熱膨張係数が原因で、酸化エルビウム被覆に微小亀裂が発生することを突き止め、JLF-1基板で被覆の性能が劣る原因を明らかにした。Zhang氏は熱力学特性と反応速度の検討から、酸化熱処理時の酸素分圧を下げることで酸化鉄の発生を抑制できると予測し、被覆の改良試験に取り組んだ。

Zhang氏は、熱処理を10ppmの酸素不純物を含む低酸素分圧のアルゴンガス雰囲気で行う事により、JLF-1の酸化鉄層の発生が抑えられ、酸化クロム中間層が生成すること、これにより酸化エルビウム被覆の水素透過低減機能が大きく向上することを確認した。Zhang氏はさらに熱処理温度と酸素分圧を系統的に変えた実験を行い、酸化鉄層発生を防ぐ条件を求めるとともに、内部から表面へのクロムの拡散と表面での酸化反応の速度の大小により酸化物の組成が定まる、とのモデルで実験結果を説明できることを明らかにした。このように熔融塩ブランケットのトリチウム透過低減被覆への適用の有効性が確認されたが、液体リチウムブランケットのMHD圧力損失低減被覆への適用には、酸化クロム中間層の形成により液体リチウムとの共存性も向上するものの、その耐食性能は不十分であった。詳細な表面観察により、この原因は、低酸素分圧で焼成を行うため、錯体の酸化分解が不十分で、残存炭化物不純物がリチウム腐食を誘発するためであることを明らかにした。これらの結果に基づき、今後の更なる改良の指針として酸素分圧の一層の最適化、基板表面のCr富化などが示唆された。このようにZhang氏の研究は、独創性が高く、核融合ブランケットの開発に寄与するとともに、被覆形成過程の原理に基づく高度化を提言するもので、学術的にも意義のあるものである。以上により、本論文は学位論文として十分価値があると判断した。

8月4日に開かれた審査委員会において、Zhang Dongxun氏は提出論文の内容を詳細に説明した。審査委員から、錯体分解により発生する不純物の効果、熱サイクル効果、想定される寿命、Cr富化の方法など材料開発に関する質問、中間層形成の原理、重水素透過抑制の発現メカニズム、リ

チウム腐食の反応過程など、基礎原理に関わる質問などが出され、広範な質疑が行なわれた。Zhang氏は各質疑において的確な返答を行なった。質疑を通じて、核融合炉ブランケットにおけるセラミックス被覆の役割と課題を良く理解していること、実験の精度向上のために多くの工夫を凝らしていること、材料内の物質移行、反応過程を深く理解していることなどが示された。

8月30日に行われた公開発表会において、研究の背景、目的、特徴、方法、実験結果とその解析、結果の位置づけと将来展望などについて約1時間の発表が行なわれ、引き続き出席者による質疑応答が行われた。ここでも明確な発表と質問に対する的確な回答がなされた。

発表論文としては、査読つき英語論文（第一著者）として3編が印刷中である。また、国際会議でのポスター発表も3回行なっている。審査会における英語の発表や質疑応答、提出された英文の博士論文からも、出願者が十分な語学力と研究能力を持っていることが認められた。

以上の結果より、本審査委員会は出願者が試験に合格であると判断した。