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学位論文題目 Development of Insulating Coating on Vanadium Alloys
for Liquid Lithium Blanket of Fusion Reactors

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論文内容の要旨

Among the concepts for breeding blanket of fusion reactors, self-cooled Li/V blanket, in which vanadium alloy acts as structural material and liquid lithium as both tritium breeder and coolant, is thought to be particularly attractive. Lithium has high tritium breeding capability, good heat transfer and negligible neutron damage. In addition vanadium alloys have low induced radioactivity, good compatibility with lithium, good resistance to neutron damage and high strength at high temperature. These advantages lead to a simple structural design, no use of neutron multiplier beryllium with enough tritium breeding rate, and continuous handling of chemistry for the breeder.

One of the critical issues for liquid Li/V-alloy blanket concept is large magneto-hydrodynamic (MHD) pressure drop against pumping system while liquid lithium flows in blanket ducts in a strong magnetic field. A promising way to mitigate the pressure drop is to apply electrically insulating coating (oxide or nitride ceramics) onto inner wall of the structural ducts.

In-situ formation of oxide coating onto vanadium alloys in liquid lithium is quite attractive because the process will make it possible to deposit coatings onto complex surfaces after fabrication of the components, and it offers the possibility to heal cracks of coatings without disassembling the components. In this method, the vanadium alloy substrate pre-charged with oxygen is exposed in liquid lithium doped with metal, where the oxygen reacts with the metal to form an insulating oxide coating on the vanadium alloys.

Among candidate coating materials, Er_2O_3 ceramics showed good compatibility with liquid Li, a high electrical resistivity, and a high stability in air with moisture, and thus is regarded as a promising candidate material for the insulating coating.

The purpose of this study is to develop an in-situ Er_2O_3 insulating coating method to V-4Cr-4Ti (NIFS-HEAT-2) that is one of the reference vanadium alloys.

For this purpose, the first step is to pre-charge oxygen with proper level and to distribute in the limited depth of V-4Cr-4Ti, without degrading mechanical property of the substrate. In the present study, the oxygen behavior in V-4Cr-4Ti during oxidation and subsequent annealing were investigated first at all. V-4Cr-4Ti alloy was oxidized in flowing Ar with impurity of oxygen, nitrogen and moisture for 0.5-8h and subsequently annealed in vacuum for 16h at 700°C. By oxidation for supplying enough oxygen, the oxygen of 1000-9000ppm was introduced into V-4Cr-4Ti with little nitrogen, where oxygen was concentrated in a region near the surface. The weight gain obeyed a parabolic law indicating that the oxidation process was controlled by thermo-diffusion rate of oxygen in V-4Cr-4Ti. During the annealing for keeping the oxygen in the substrate, oxygen was homogeneously diffused into depth of 150 μm . The diffusion depth of oxygen in V-4Cr-4Ti is limited because of Ti-O net precipitates formed as oxygen trap. Ti-O is expected to dissolve supplying free oxygen for forming the coating during the subsequent

exposure to liquid Li. The study indicated feasibility to control the level and distribution of oxygen in the surface region of V-4Cr-4Ti. The optimized parameters of pre-charging oxygen into V-4Cr-4Ti for forming in-situ oxide coating are oxidation in Ar (700°C, 6h) followed by annealing in vacuum (700°C, 16h).

The second step is chemical formation of Er₂O₃ coating on V-4Cr-4Ti during exposure in liquid Li doped with Er. In the present study, V-4Cr-4Ti were oxidized at 700°C for 1-8h, annealed at 700°C for 16h, and finally exposed for 100 h at 600°C. By the exposure, the Er₂O₃ layer was formed on V-4Cr-4Ti oxidized plus annealed, but was not formed on those either as-received or oxidized only. The resistivity of V-4Cr-4Ti with Er₂O₃ coating is $\sim 10^6 \Omega\text{m}^2$ which is much larger than the minimum requirement ($\sim 10^{-2} \Omega\text{m}^2$). The results indicate that the in-situ formation of Er₂O₃ coating is viable, the oxygen source to form coating is the pre-charged oxygen in V-4Cr-4Ti, and that the annealing after oxidation to homogenize oxygen distribution in substrate is necessary for the formation of the coating.

The third step is to characterize and investigate the potential long-term stability of the Er₂O₃ coating. V-4Cr-4Ti substrate was oxidized in flowing Ar at 700°C, annealed in vacuum at 700°C, and finally exposed to liquid Li doped with Er from 500°C to 700°C. The oxygen charged and homogenized in limited depth of the substrate was stored as Ti-O net precipitates. It was verified that Ti-O dissolved to release oxygen at high temperature acting as an oxygen source. The surface layer formed on V-4Cr-4Ti consists of double sub-layers, namely an insulating coating of Er₂O₃ and an intermediate layer of mixed ErN and V-compounds. The Er₂O₃ coating was found to be stable up to 750h of exposure time in liquid lithium doped with erbium at 600°C with its saturated thickness of $\sim 0.1\mu\text{m}$, stable up to 300h at 650°C with saturated thickness of $\sim 0.6\mu\text{m}$, and stable up to 300h at 700°C with saturated thickness of $\sim 1.3\mu\text{m}$. Cracking of coating can be avoided during the Li cleanout process after exposure by using weak lotion (liquid NH₃) at low temperature (-33.5°C). Thus it is inferred that no cracks were formed during the exposure in liquid Li. By re-exposure of intentionally cracked coating in liquid Li doped with erbium, the potentiality of self-healing to cracks was shown. The coating once formed in Li doped with erbium at 700°C was stable in pure Li at 700°C, thus demonstrating the stability of Er₂O₃ coating in liquid Li. The lower limits of the Er doping level to form Er₂O₃ coating were experimentally gotten to be in the range of 1–2.5wt%(0.04–1at%) and at exposure temperature higher than 500°C. The limit is expected to be much lower with reduced level of the dissolving oxygen in liquid Li. The in-situ measurement of resistivity during heating in vacuum showed that the coating had resistivity over minimum requirement ($10^{-2} \Omega\text{m}^2$) up to 550°C. The resistivity satisfying the requirement to higher temperature is expected to show with improved measurement apparatus.

Finally, the mechanisms for nucleation and growth of the coating were investigated. By oxidation and annealing, the oxygen was charged into substrate to form Ti-O net phase as oxygen source to the coating. The surface layer formed on V-4Cr-4Ti consists of two sub-layers, insulating Er₂O₃ coating and intermediate layer of mixed ErN and Er-V-O. The

durations of nucleation at 600, 650 and 700°C are experimentally proved to be quite short. The measured growth rate showed the kinetics of logarithmic law with high exponent ($n \approx 3$ or 4) at 600°C and 650°C, suggesting that the rate of growth to Er_2O_3 coating should be very low. The growth was expedited suddenly at 700°C resulting in low exponent ($n \approx 2$) that almost obeys parabolic law. A phenomenological model was proposed for mechanism of the coating kinetics, which showed growth of Er_2O_3 coating is controlled by diffusion of oxygen and delivery of erbium to interface between the vanadium alloy substrate and the liquid lithium. The model also showed impurity transport across the interface and formation mechanism of the resulting intermediate layer.

In summary, this study has demonstrated that in-situ Er_2O_3 coating on V-4Cr-4Ti in liquid Li doped with erbium is a viable technology. Coating was stable at 600°C to 750h and at 700°C to 300h. Coating showed satisfactory resistivity to minimum requirement for reducing MHD pressure drop. Coating showed self-healing potentiality. The kinetics of the coating showed quick nucleation followed by growth with logarithmic law. The phenomenological modeling showed formation mechanism of the observed intermediate layer.

論文の審査結果の要旨

核融合炉においてブランケットは、中性子エネルギーの熱変換と燃料トリチウムの増殖というきわめて重要な機能を課せられたシステムであり、その高度化は核融合炉のエネルギー発生装置としての高度化に直結するものである。本論文で対象とするのは液体リチウムを増殖材、冷却材に用い低放射化バナジウム合金を構造材に用いるシステムで、一種類の流体により増殖・冷却が可能であること、中性子増倍用ベリリウムが不要であることなどにより、単純構造の設計が可能で、先進ブランケットとして大きく期待されている。一方、このシステムは、強磁場下で導電流体を流すことによって生じる電磁流体力学的(MHD)圧力損失が問題となり、液体リチウムの腐食に長期間耐える絶縁被覆の開発が中心的な課題である。これまでいくつかのセラミックスが候補に挙がり開発が進められてきたが、有望な被覆システムを選定するには至っていないのが現状である。

姚振宇君は、この絶縁被覆開発研究をテーマとし、酸化エルビウムのその場被覆法の開発とその基礎機構の研究に取り組んだ。その場被覆法はリチウム中に予め金属を溶し込み、バナジウム合金に予注入した酸素と高温で反応させ、表面に絶縁被覆を形成する方法で、複雑形状の被覆が可能であり、自己修復性が見込める魅力ある被覆法である。アメリカでは以前酸化カルシウムによる開発が進められたが、被覆の安定性が不足したため開発が中断した。姚君は、バルク材のリチウム腐食試験により酸化エルビウムが優れた耐食性を有することが示された最近の成果に注目し、初めての試みとして、酸化エルビウムによるその場被覆法の開発に取り組んだ。姚君はリチウム浸漬被覆試験装置の設計製作、被覆に先立つ基板の表面酸化処理条件の最適化、被覆の様々な分析機器を駆使した評価、などの実験に集中して取り組んだ。被覆形成の温度条件、酸素注入条件依存性を示すとともに、形成した被覆が600℃で約1000時間まで液体リチウム中で安定であることを示し、本被覆法のフィージビリティを明確に示した。また、被覆および基板の詳細な分析・観察により被覆の基礎機構を明らかにした。特に、被覆が安定形成する酸素予注入条件においては、基板バナジウム合金中にチタン酸化物析出の網状組織が形成され、その結果酸素を長期間保持する能力を持つ事を示したのは、今までの経験的な最適化研究に対し、微細組織の観点から機構を明らかにした点が高く評価される。姚君はまた、さまざまな実験の工夫により、一度形成した被覆がリチウムの純度に関わらず安定であること、表面に傷を加えても絶縁層を再形成し修復することを示し、本手法の有用性を明らかにした。

姚君はさらにモデル研究にも取り組み、被覆層の形成成長が基板バナジウム合金中の溶存酸素の表面への拡散に律速すること、液体リチウムから基板バナジウム合金中に窒素と金属エルビウムが侵入し、被覆層下に第二層を作り、被覆の安定性の向上と酸素の液体リチウムへの溶出の抑制に寄与していることなどを明らかにした。これらのモデルに基づき、一旦低温で緻密な被覆層を形成させてから目標温度での被覆の成長を行う、液体リチウムからの窒素の侵入量を調整するため液体リチウム中の窒素不純物濃度を適正值に保つ、など一層の高度化に向けた指針を明らかにした。

以上本研究は、核融合先進システムとして期待される液体リチウム・バナジウム合金ブランケットの重要な開発課題であるMHD絶縁被覆に関し、酸化エルビウムその場被覆法の適用の見通しを明らかにするとともに、被覆形成成長について酸素の挙動と微細組織変化

に基づく基礎メカニズムを示し、被覆の長期安定化に向けての指針を明らかにした。これらは核融合ブランケット開発研究に寄与するものであるとともに、学術的にも意義のある研究と認められる。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。