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Ferritic/Martensitic Steel with Liquid

lithium

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Development of breeding and structural materials for blankets is the key issue of fusion reactors. Fe-Cr-W based RAFM (Reduced Activation Ferritic/Martensite) steels are widely regarded as promising blanket structural materials, because of its low activation properties, radiation resistance and industrial maturity. Blanket concepts with liquid lithium (Li) breeder/coolant provide attractive options for high tritium breeding ratio, high efficiency and simplicity of blanket system.

One of the critical issues for RAFM/Li blanket is the compatibility of RAFM steel with liquid Li. As to the corrosion of ferritic steels in Li, only studies on conventional Fe-Cr-Mo are available. In those studies, however, investigation on microstructure and micro-chemical processes are quite limited. Any data are not available for RAFM (Fe-Cr-W) steels yet.

The purpose of the present study is to examine the compatibility of RAFM steels with liquid Li with respect to corrosion rate and the degradation of mechanical properties and to clarify the underlying mechanism based on the element transfer and change of microstructure during the corrosion process.

In this study, the compatibility of JLF-1(Fe-9Cr-2W-0.1C), a RAFM steel developed in Japan, with static and flowing Li was investigated. The coupon specimens (16×4×0.25mm) were exposed in an isothermal pot for static tests and thermal convection SS316 (Fe-Cr-Ni) loop for flowing tests. After exposure, the corrosion characteristics were examined by fine scale weight measurement, SEM/EDS (Scanning Electron Microscope/Energy Dispersive X-ray Spectrometer), TEM (Transmission Electron Microscopy) and Vickers hardness test.

In the static test, the weight loss of JLF-1 specimens increased with temperature. After exposure at 700°C for 100h, JLF-1 specimens suffered severe corrosion and the corrosion rate was 0.18mm/yr. The kinetics of weight loss at temperature of 500°C and 600 °C showed that the corrosion of JLF-1 became saturated with the exposure time. This is possibly due to the formation of saturated layer of dissolved elements in liquid lithium near the specimen surface. In the corrosion test in a thermal convection loop, the corrosion rate at 500°C for 250h was significantly larger than that obtained in the static test in an identical condition. After Li exposure, the phase transformation from martensite to ferrite was found on the samples. This is the first time that the phase change from martensite to ferrite is observed after Li attack. The chemical analysis results and the depletion of carbides suggested that the phase change was caused by the depletion of carbon. At the same time, selective depletion of other alloy elements, such as Cr and W, was detected by EDS on the surface. Vickers hardness results showed that obvious softening occurred on the surface of the specimens after Li exposure and the depth of the softened region was consistent with that of the phase transformation. The flowing Li enhanced the weight loss, phase change and hardness reduction due to the mass transfer.

The influence of alloy composition on the corrosion was investigated by comparing the corrosion behavior of JLF-1, binary Fe-Cr and pure iron at 700°C for 100hr. The corrosion of JLF-1 is more significant than that of Fe-9Cr and pure iron at 973K. The selective dissolution of

Cr, W and C into lithium seems to enhance the corrosion. Significant phase transformation from martensite to ferrite to the depth of 100, m was observed on the JLF-1 specimens after exposure in Li at 700°C for 100h. The phase change resulted in drastic hardness drop from 250 to 140Hv. For the Fe-9Cr, the softened layer (~5, m) was found on the surface of the specimen after Li attack due to the depletion of Cr and W. This was verified by the EDS line scan on the cross section of specimens. No mechanical change was observed on the pure Fe specimen before and after exposure.

To study the influence of container materials, the coupon specimens of JLF-1 were exposed in Mo, SS316 and Nb crucibles separately at 600°C for 250h. The corrosion characteristics in different crucible were compared. After exposure, the specimens exposed in Mo and Nb crucible lost weight, while the specimens in SS316 crucible gained weight due to the precipitation of Ni dissolved from crucible materials. The phase transformation was observed on cross section of specimens exposed in Nb crucible (~20, m) and Mo crucible (~10, m). No phase change was found in the case of SS316 container. The phase change caused a corresponding reduction of hardness on JLF-1 samples in depth. It is clear that the Nb container enhanced the depletion of carbon and the phase transformation by trapping C and achieving a very low C concentration.

Analysis of the experimental results was carried out based on the thermodynamic and kinetic modeling. The results showed that the driving force of corrosion is the level of Fe and Cr in Li. Saturation of those elements in Li results in the suppression of corrosion. However, production of compounds of N, Li and alloy elements was shown to determine the level of Fe and Cr in Li. The loss of C leads to the phase change. The driving force of decarburization is the level of C in Li. The trapping of C by the container materials can enhance the phase transformation. The diffusion of C in the martensite controls the extension of phase change region.

In conclusion, expected influences of Li attack to RAFM steel are the loss of materials by dissolution of the constituent elements and the degradation of mechanical properties caused by phase transformation from martensite to ferrite as the result of dissolution of C. Based on the data obtained, the compatibility of RAFM steel in Li seems not to be a serious issue once the level of N in Li is kept low. The phase transformation will be reduced by avoiding the use of materials which has high affinity with C.

## 論文の審査結果の要旨

核融合炉ブランケットの開発において、構成材料間の両立性は重要な研究開発課題である。特に、液体金属や溶融塩を増殖材や冷却材に用いる液体増殖ブランケットでは、腐食による構造材の損失や特性劣化がブランケットの使用温度領域や交換頻度に重大な影響を及ぼすことが懸念されている。腐食特性は温度分布、流動環境、不純物などの影響を強く受けることから、信頼性の高い腐食評価を行い耐食性を向上させるには、構造材料と増殖材の間の物質移行を明らかにすることが重要である。Qi XU 氏の研究は、このようなブランケット開発における重要課題に対して基礎学術的な視点からの貢献を目指したものである。

Qi XU 氏は、近未来の実用化に向けて開発が進められている低放射化構造材候補材で ある「低放射化フェライト・マルテンサイト鋼(RAFM)」と、トリチウム増殖能、熱除去 効率などに優れた増殖・冷却材候補である「液体リチウム」を組み合わせたブランケット を取り上げ、両者間の物質移行の観点から両立性に関する研究を行なった。反応性の高い 液体リチウムの静的及び流動環境での腐食特性を求める試験装置を設計製作し、RAFM の 腐食損失、腐食による組織変化、組成変化を明らかにした。特に、液体リチウムの脱炭作 用により RAFM 表面近傍がマルテンサイト相からフェライト相に変質し軟化が起こるこ とを示し、腐食損失だけでなく強度低下も問題になることを明らかにしたことは、これま でにない新しい知見である。流動環境では静的環境に比べ腐食が促進されることはこれま で別の材料で報告されていたが、脱炭と相変化も促進されることを示したことの意義も大 きい。実験において腐食試料の局所組成変化をエネルギー分散型X線分光器などを駆使し て精密に求めるとともに、モデルを立てて RAFM 中の物質移行、RAFM と液体リチウム との間の物質移行過程を明らかにした。特に、腐食損失の実験データが、液体リチウム中 の溶融窒素不純物と構造材料成分元素との化学反応による流出として定量的に説明でき、 リチウム中の溶融窒素不純物の低減により腐食損失を大幅に低減できること、腐食試験に 用いる容器材料が炭素と親和力が強いとリチウム中の炭素濃度が低く維持されるために試 料の脱炭および相変化が促進されること、相変化領域の成長が炭素の構造材内部での拡散 で支配されることなどを熱力学および反応方程式の解析により示したことは、腐食機構の 解明に寄与しただけでなく、耐食性向上に向けた具体的な指針を示した重要な成果である。

以上本研究は、高性能かつ近未来に実現可能と期待される低放射化フェライト・マルテンサイト鋼と液体リチウムを用いたブランケットについて、その腐食挙動を支配する物質移行過程を明らかにし、新しい現象を示して問題提起を行なうとともに、耐食性向上に向けての見通しを明らかにしたものである。これらの成果は核融合炉ブランケットの開発に大きく寄与するとともに、液体金属腐食の研究分野で学術的に意義ある研究であると認められる。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。