§6. Compatibility of Structural Materials with FLIBE

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A molten salt mixture of LiF-BeF_2 (FLIBE) is considered as a candidate for tritium breeding material in a liquid blanket system, and the corrosion behavior of FLIBE against structural materials is a critical issue for the system design. However, the database is still very poor and more experimental data are strongly required. As a fundamental research, this work aims to elucidate the process and mechanism of the corrosion under static conditions at high temperature by both experimental and theoretical studies.

The corrosion behavior of FLIBE against structural materials has been studied for, e.g. Ni-based alloys, which were practically utilized for the core container of Molten Salt Reactor Experiment (MSRE). In general for molten salt corrosion, impurities in the system tend to play an important role. As for FLIBE blanket system, HF, H_2O and O_2 would be generated under neutron irradiation, and their chemical behavior should be investigated thoroughly. Ferritic steel (JLF-1) and V-based alloy are supposed to be used as the structural material in FFHR, but no experimental study is found for these materials up to the present. Moreover, almost nothing is known about their compatibility with FLIBE under a metallic-beryllium-coexisting system, in which a high reduction condition may be realized. Thus, the followings were carried out; 1) thermochemical calculation for screening practical conditions in experimental systems and 2) preliminary dipping experiment.

In the computational study, the compatibility of structural materials with FLIBE under an atmosphere containing HF, H_2O, and O_2 was simulated using an integrated thermochemical data base system, MALT2[1,2] and an attached Gibbs free energy minimizer, gem code[3] for the calculation of chemical equilibrium. It was found that structural materials would be ready not to be fluorinated but to be oxidized if oxidizing species existed. The constituents of FLIBE itself and its atmosphere under neutron irradiation were estimated in consideration of nuclear transmutation for arranging the definitive condition for experimental study. Though fluorination was found under the atmosphere containing HF, structural materials such as JLF-1, V-based alloy and molybdenum would have sufficient corrosion-resistance when those oxides functioned as protective scales. Moreover, it was confirmed that the addition of metallic beryllium is very effective for removal of corrosive species, and that structural materials are not attacked at all in beryllium-added systems. However, these expectations should be confirmed by experiment from a kinetic point as well as a thermodynamic point of view.

In the experiment, SUS430 ferritic steel (Fe-18Cr) and pure vanadium were examined on corrosion-resistance against molten FLIBE. Lithium fluoride (LiF) of 99.9% in purity and beryllium fluoride (BeF_2) of 99.5% supplied by Furuuchi Chemical Corporation were used to prepare the fluoride mixture. Dipping experiments were performed in a glove box of Ar atmosphere. Molybdenum crucibles were used as containers, in each of which a test specimen was put with fluoride components weighed to be a 2:1 mixture of LiF and BeF_2 and dried at 673K for about 3 hours. Then, the crucible including the specimen in molten FLIBE was kept at 823K for another 3 hours. A trace of moisture had been adsorbed on the surface of the salts, and a trace of HF generated on melting should have been contained in the system. After the test, the specimen was taken out of the molten salt and analyzed by XRD and RBS.

No severe corrosion was observed for SUS430 and it was confirmed that Cr_2O_3 and $FeCr_2O_4$ were formed on the surface. This means that the oxides may survive in FLIBE and work as protective scales. In case of vanadium, on the other hand, quite severe corrosion was observed; a lot of black particles were generated and flown out with FLIBE convection. PIE results showed fluorine invasion into vanadium and subsequent fluoride formation (VF_2). In order to improve the compatibility of vanadium, the addition of corrosion-resistant element, Be utilization as a REDOX buffer, and corrosion resistant coating should be investigated.

References

1) S.Yamauchi: Netsu Sokutei 12 (1985) 142
2) H.Yokokawa: Netsu Sokutei 12 (1985) 144
3) T.Matsumoto et al.: Netsu Sokutei 19 (1992) 170