

Investigation of corrosion control technologies for structural materials in MSR

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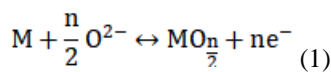
1. Introduction

A molten salt reactor (MSR) dissolves nuclear fuel in molten salt and uses it as a coolant and nuclear fuel. Generally, MSR is safer than conventional reactors as it isn't likely to occur loss-of-coolant accidents, and also, advantageous for proliferation resistance and nuclear transmutation. In addition, it is expected to make a small-size reactor with its remarkable thermal efficiency and simple structure, so it receives attention as a small nuclear plant. One of the big problems of the MSR is molten salt corrosion and corrosion in structural materials can affect the life and safety of nuclear plants. Furthermore, there is a concern that an increase of impurities in the salt during corrosion, results in the deterioration of the reactor's performance. Therefore, corrosion control technologies for MSR are widely researched for the safety, performance, and life of MSR.

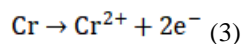
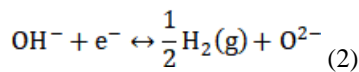
2. Characteristic of salt corrosion

2.1. Corrosion by water and oxygen

Corrosion of the structural material can be expressed as the oxidation of metallic elements which generates M^{n+} ions and electrons from the metallic M element. One of the reasons for molten salt corrosion is oxide impurities. Corrosion due to oxide ion is produced by the following reaction equation.

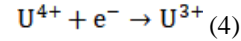


Water ingress also can cause corrosion [1]. Water ionizes into H^+ , OH^- , and O^{2-} ions which can cause corrosion as shown in the above equation. This eventually leads to the corrosion of structural materials. OH^- ion also can be reduced into O^{2-} ion by oxidizing structural material.



2.2. Corrosion due to salt potential

If the potential of some material is larger in a positive direction than the oxidation potential of the structural material, the structural material acts as a reducing agent, oxidizes and, in turn, corrosion occurs. A typical example is structural material corrosion by U(IV)/U(III).



The potential of this reaction is higher positively than the redox potential of the structural material, so U^{4+} becomes an oxidizing agent and structural element such as Cr oxidizes, causing corrosion.

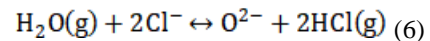
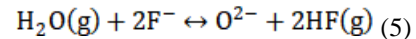
2.3. Corrosion by fission products

Fission products (FPs) generated during the fission process can cause corrosion and one of the representative elements is Tellurium (Te). Because Te is in the same group as O and S, it can act as an oxidizing agent. It is reported that Te can provoke intergranular cracking (IGC) in Ni-based alloy chemically and electrochemically.

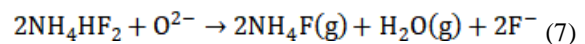
3. Corrosion Control Technology

3.1. Salt purification

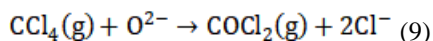
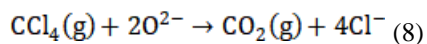
One of the promising strategies to mitigate molten salt corrosion is eliminating the impurities from the salt. It is reported that the decrement of the moisture and oxygen content in the salt can reduce corrosion. Generally, water in salt can be eliminated by thermal treatment with Ar gas blowing or vacuum condition. It is reported that this is effective not only to remove water but also to remove oxide ions. When HF or HCl is injected into the salt, the effect of removing oxide can be maximized.



Reverses of the above two reactions indicate that they consume oxides and produce water and F^- or Cl^- [2]. The formed water vapor may be removed by applying the heat described above. At this point, injecting HF/ H_2 or HF/ H_2 /Ar rather than injecting pure HF into fluoride salts is recommended because H_2 makes the salt less oxidizing. For the fluoride system, using solid NH_4HF_2 instead of gaseous HF is also recommended for safety and convenience.



As shown in the formula above, the mixture of NH_4HF_2 and fluoride salt consumes oxides and releases NH_4F gas and water vapor. For the chloride salt system, CCl_4 can be applied to remove residual oxide ions [3].



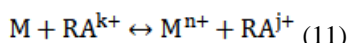
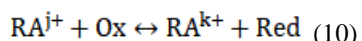
3.2. Reducing agent injection

Introducing a sacrificial metal can be an option to protect structural material. For the FLiBe system, it is reported that the corrosion rate was effectively reduced when after the Be injection. Specifically, it was found that the amount of Cr and Fe dissolved in the salt was remarkably reduced by short-immersing the Be rod [4]. This is due to the sacrificial effect of Be metal that can be seen to significantly reduce the concentration of HF in the effluent gas while Be inputs and Be rods are corroded.

Unlike dissolved salt control methods, major metal control methods are suspected to have insufficient effect if it is far from injected Be metal, but there is dissolved Be with sufficient solubility in FLiBe and it is enough to control redox potential. It was also studied to apply a major metal control method to chloride salts with Mg in the MgCl_2 -KCl salt. Zr is also proposed as a redox buffer agent in a fluoride salt system where Be is not used. However, when Zr was used as a buffer agent, the formation of a coating composed of Ni/Zr intermetallic compounds in FLiNaK was reported.

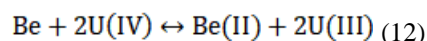
3.3. Redox potential control

The concept of redox potential control is to introduce another redox pair $\text{RA}^{k+}/\text{RA}^{j+}$ ($k > j$) to help the salt to be less oxidizing. When $\text{RA}^{k+}/\text{RA}^{j+}$ is introduced, the equilibrium of the reaction will be affected by the below reactions.

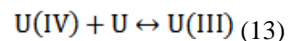


In these reactions, movement of corrosion potential to a negative direction occurs and the oxidation rate of RA^{j+} becomes larger than the dissolution rate of metal M. This shows that most oxidizing agents are used to oxidize RA^{j+} rather than corroding structural materials. Compared to the major metal control method, the dissolved salt control method is more attractive because throughout the molten salt system, dissolved RA is uniformly spread, and the method doesn't form intermetallic compounds.

One of the things which can utilize the method is U(IV)/U(III). In terms of electrode kinetics, the U(IV)/U(III) reaction can be used as a redox buffer because the U(IV)/U(III) reaction has a higher exchange current density than the metal dissolution reaction. Corrosion is suppressed as U(III) is oxidized instead of the metal. The decrease in consumed U(III) concentration can be solved by contacting Be.



U(IV) can be reduced to U(III) since the redox potential of Be(II)/Be has a more negative value. Using U metal to control the concentration ratio is also being studied [5].



Due to the above reaction, consumed U(III) is generated and the concentration ratio can be maintained. In addition to U(IV)/U(III), the use of redox pairs Eu(III)/Eu(II) for corrosion control in structural metals is also being studied. When comparing the oxidation potential of Cr, which is easily corroded, and the formal standard potential of Eu(III)/Eu(II), it was found that adjusting the concentration ratio below 0.05 can mitigate Cr corrosion. In addition, the concentration control approach is reasonable because Eu metal deposition can't occur as the potassium deposition potential in FLiNaK is more negative than the potential of Eu(II)/Eu when the salt is over-reduced. Sm(III)/Sm(II) and Yb(III)/Yb(II) are also possible pairs that can be used as the dissolved salt control method.

4. Conclusion

The investigation showed that a considerable number of studies have been conducted on the corrosion of MSR structural materials, and many techniques have been studied to control corrosion. However, it was also found that most of the technologies mentioned above were studied in fluoride salts such as FLiNaK and FLiBe. It is believed that developed corrosion control techniques based on the fluoride system can be adjusted to the chloride salt system but need to be strictly analyzed to figure out the dissimilar behaviors.

ACKNOWLEDGMENT

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