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Journal of Nuclear Materials 258–263 (1998) 513–518

journal of nuclear materials

# Compatibility of structural materials with $Li_2BeF_4$ molten salt breeder

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**Abstract**

Compatibility of structural materials (ferritic steel, vanadium-based alloy and molybdenum) with molten LiF–$BeF_2$ mixture under the atmosphere containing $O_2$, $H_2O$ and HF was studied using thermodynamical calculation of chemical equilibria at 823 K. It was clarified that the oxidation of structural materials would have precedence over fluorination with coexistence of oxidizing species though fluorination was found under the atmosphere containing HF. Then, these materials would have satisfactory corrosion resistance if generated oxides function as protective scales. 

## 1. Introduction

A mixture of LiF–$BeF_2$, Flibe, can be considered as a candidate for tritium breeding material in a liquid blanket system of a fusion reactor. Flibe has favorable characteristics such as low electric conductivity, chemical stability, etc., and it can be utilized as a coolant.

The liquid blanket system using Flibe is utilized in the conceptual design for Force-Free Helical Reactor, FFHR [1–3]. In this design, ferritic steel (e.g. Fe–9Cr–2W) or V-based alloy (e.g. V–4Cr–4Ti) is considered to be utilized for the structural material of the blanket, as is shown in Fig. 1. Then, the corrosion of such materials is one of the critical issues; the compatibility of structural materials with molten fluoride strongly influences the durability of the system.

In the present work, compatibility of materials with Flibe was estimated using thermochemical calculation under the conditions which are difficult for us to control practically in experimental systems.

## 2. Thermochemical calculation

### 2.1. Thermodynamical data

Recent integrated thermochemical database systems enable us to calculate complex chemical equilibria. In this work, thermodynamic database system, MALT2 [4,5] was utilized for the calculation of chemical equilibria for Flibe/structural material systems.

Flibe itself has higher chemical stability as a fluoride than those of ordinary metals which would be put to practical use for fusion reactors, and has almost no reactivity with structural materials. In case of this work, however, Flibe generates tritium under the neutron irradiation, so a corrosive species TF (is equivalent to HF chemically) should be taken into account. Moreover, $BeF_2$ hygroscopic and deliquescent and HF is also generated at elevated temperatures as follows:

$$BeF_2 + H_2O \rightleftarrows BeO + 2HF \quad (1)$$

Therefore, it can be thought that Flibe containing moisture causes corrosive circumstance.

### 2.2. Computational conditions

In this work, *gem* code [6] attached to the database system MALT2 was applied as the Gibbs free energy

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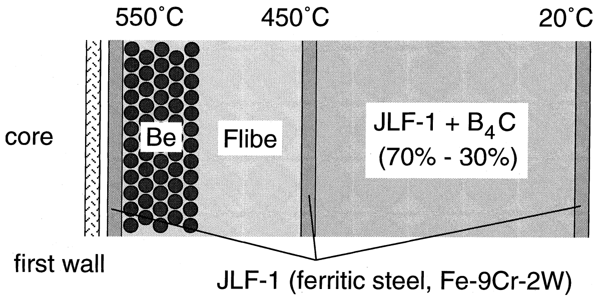


Fig. 1. Conceptual design of FFHR blanket.

minimizer. In this code, the total free energy of the multi-component system is described as a summation of ideal entropy of mixing for gas phase and distributed Gibbs free energy divided by $RT$ of each component as a pure substance in proportion to its fraction

$$G_{\text{total}} = \sum_i \frac{g_i}{RT} x_i + \sum_{j \text{ for gas phase}} x_j \ln \frac{x_j P/\text{atm}}{\sum_{k \text{ for gas phase}} x_k}, \quad (2)$$

where $P$ is the total pressure of the system (1 atm in this work), $x_i$ is the mole fraction of component $i$ and $g_i$ is the Gibbs free energy per mole of component $i$ as a pure substance. Consequently, neither the solubility of various species to Flibe nor non-ideal reduction of activity of components was taken into consideration.

The calculated system is shown schematically in Fig. 2; 10 mol of gas phase which consists of inert gas and impurities and/or additives such as $O_2$, $H_2O$ and HF; 10 mol of condensed phases which consist of 9 mol of fluoride mixture (6 mol of LiF and 3 mol of $BeF_2$) and 1 mol of metallic material. Influence of impurities such as oxygen and moisture was simulated through addition of these components to the gas phase. Oxygen fraction was fixed to be 2 mol/ppm (ordinary impurity level for inert gas cylinders) or 100 mol/ppm (more oxidizing case), and the amount of $H_2O$ was varied from the order of ppm to percent. Influence of excess HF was also simulated in consideration of the condition of liquid blanket of a fusion reactor. Temperature of all calculated systems was fixed to be 823 K.

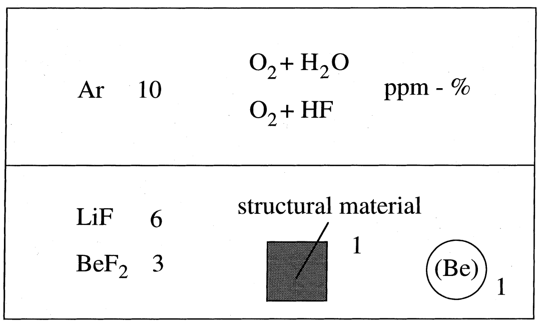


Fig. 2. Schematic drawing of the simulated system.

## 3. Results and discussion

### 3.1. Ferritic steel

Fig. 3(a) shows the effect of the initial amount of $H_2O$ to the product system. Fluorination of ferritic steel Fe–9Cr–2W was not found under the $O_2$–$H_2O$-added atmosphere except in case of very large $H_2O$ fraction; the steel seemed to be merely oxidized by $H_2O$ in spite of coexistence of Flibe.

Ferritic steel can be considered to have good compatibility with molten Flibe under the atmosphere containing oxygen if the amount of moisture is properly controlled. In case of Fe–9Cr–2W, $BeWO_4$ was found to be generated when the amount of $H_2O$ is large, say, over 0.2% for the considered simulated system; generation of beryllium compound is not favorable, so the dehumidification of the system is important.

In the $O_2$–HF-added system, ferritic steel is fluorinated to generate $CrF_2$, as shown in Fig. 3(b). However, oxidizing species is ready to react not with Flibe to generate fluorinating gas but with chromium to generate $Cr_2O_3$. Chromium oxide is thought to function as a protective scale in practical systems, so it can be considered that ferritic steel has sufficient resistance against fluorinating circumstance containing oxidizing components. Initial content of $O_2$ only influences the amount of product $Cr_2O_3$, which is not removed by HF up to impractically large fractions of HF.

### 3.2. Vanadium-based alloy

Fig. 4(a) shows the influence of $H_2O$ to the product system. Fluorination of V–4Cr–4Ti is negligible and Ti is oxidized to TiO up to the condition under which Ti is

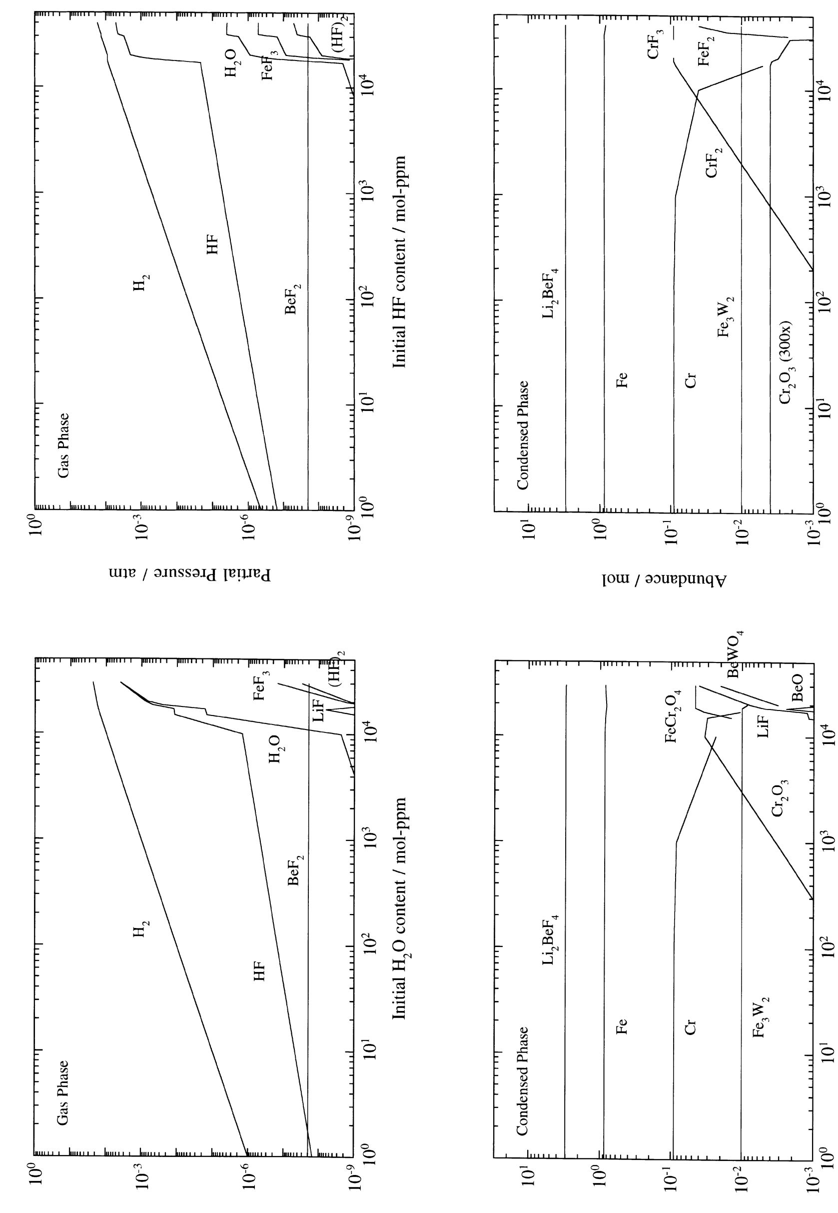


Fig. 3. Influence of the additive gas to the product system (Fe–9Cr–2W): (a) $H_2O$ addition (Ar-2 ppm $O_2$–$x$$H_2O$); (b) HF addition (Ar-2 ppm $O_2$–$x$HF).

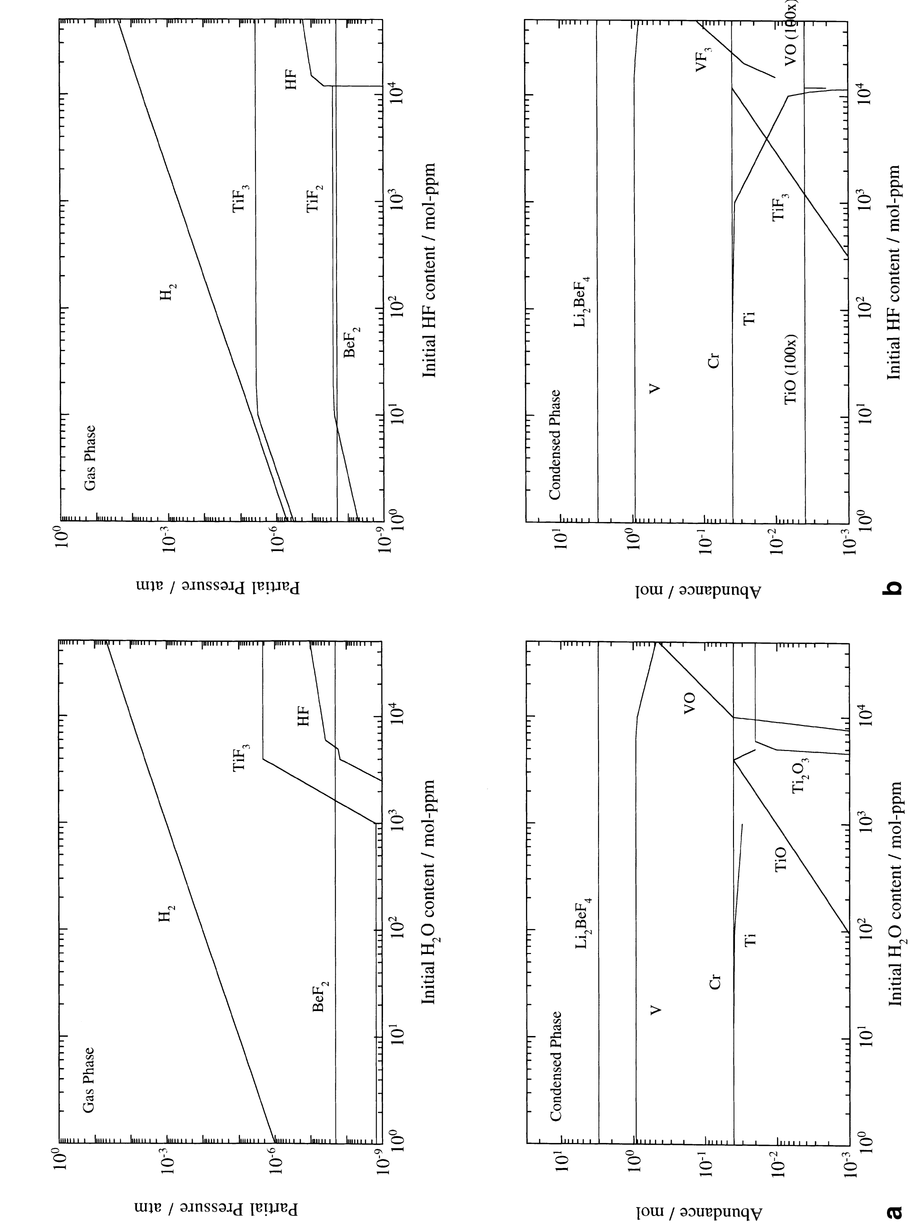


Fig. 4. Influence of the additive gas to the product system (V–4Cr–4Ti): (a) $H_2O$ addition (Ar-2 ppm $O_2$–$x$$H_2O$); (b) HF addition (Ar-2 ppm $O_2$–$x$HF).

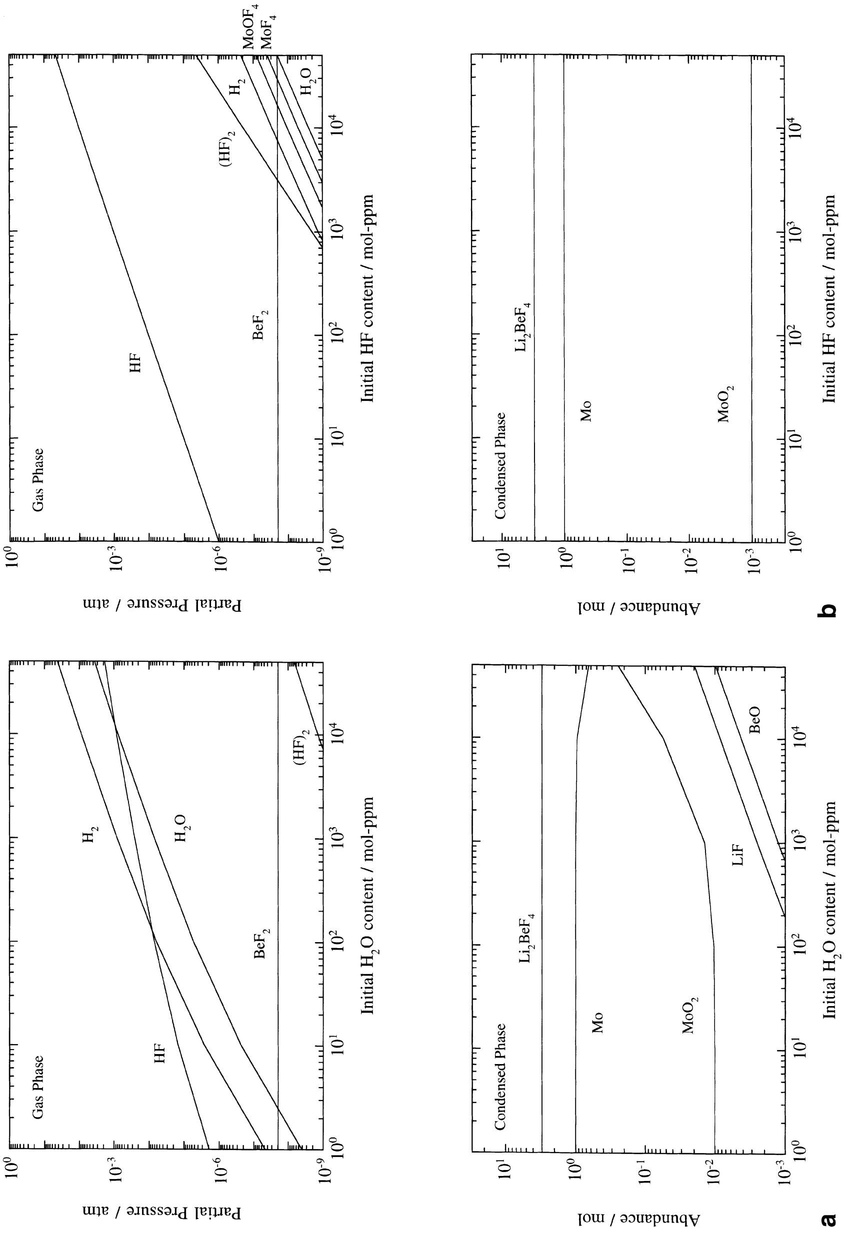


Fig. 5. Influence of the additive gas to the product system (Mo): (a) $H_2O$ addition (Ar-2 ppm $O_2$–$xH_2O$); (b) HF addition (Ar-2 ppm $O_2$–$x$HF).

depleted. Once metallic Ti is depleted, Ti(III) compounds $Ti_2O_3$ and $TiF_3$, are generated. After that, only oxidation of base metal occurs when the amount of $H_2O$ is large, say, over 0.4% for the simulated system.

In the $O_2$–HF-added system, V–4Cr–4Ti is fluorinated to generate $TiF_3$ (and $VF_3$ after the depletion of Ti), as is shown in Fig. 4(b). However, oxidizing species is ready to react not with Flibe but with Ti (and V after the depletion of Ti) to generate TiO or $Ti_2O_3$ (and VO after the depletion of Ti), just like the case of ferritic steel. Then, the V-based alloy V–4Cr–4Ti would have corrosion resistance if the oxides of Ti and V function satisfactorily as protective scales. Initial content of $O_2$ only influences the amount of oxide product, just like in the case of ferritic steel.

### 3.3. Molybdenum

As is shown in Fig. 5(a), Mo is not found to be fluorinated at all under the $O_2$–$H_2O$-added atmosphere. The reaction which occurs in this system can be thought simply as an oxidation of Mo by $H_2O$. In addition, the behavior of $O_2$–HF-added system is almost the same as that of $O_2$–$H_2O$-added system except for the generation of a little amount of $MoOF_4$ (Fig. 5(b)). It was confirmed that Mo has sufficient corrosion resistance.

### 3.4. Practical condition

In the conceptual design of FFHR blanket system, it is suggested that the addition of metal beryllium is effective for improvement of tritium breeding ratio and deactivation of corrosive specimens. Systems containing 1 mol of Be were also simulated in this work, and it was found that structural materials was not corroded at all in such systems regardless of the existence of oxygen. The products of $BeF_2$, BeO and $BeH_2$ were found.

According to the design of FFHR, ca. $10^2$ mol of tritium generation per day in ca. $5 \times 10^6$ mol of Flibe blanket is expected. Therefore, $10^4$ mol/ppm of HF (storage for about 1 yr) is enough as initial content in the simulation even if release and recovery of tritium were ignored. Moreover, it is easily expected that a practical system is more moderate, considering the reduction of activities of corrosive specimens by mixing and that the solubility of HF in molten Flibe is ca. 300 ppm/atm [7].

## 4. Conclusion

Compatibility of structural materials with Flibe under the atmosphere containing $O_2$, $H_2O$, HF was simulated using the thermochemical calculation. It was found that structural materials would be ready not to be fluorinated but to be oxidized if oxidizing species existed. Though fluorination was found under the atmosphere containing HF, structural materials such as ferritic steel, V-based alloy and molybdenum would have sufficient corrosion resistance when those oxides functioned as protective scales. Moreover, it can be considered that corrosion behavior is more moderate when the practical blanket system is taken into account.

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