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Compatibility of structural candidate materials with LiF–BeF_2 molten salt mixture

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Abstract

Compatibility of structural materials such as JLF-1 (Fe–9Cr–2W), vanadium alloys (e.g., V–5Cr–5Ti) and SiC with Flibe (LiF–BeF_2) is a key issue for the force-free helical reactor (FFHR) blanket concept. In the present study, the corrosion behavior of SUS430 (Fe–18Cr) and SiC in static Flibe was investigated as a first step. After being dipped in Flibe containing a trace of HF at 550°C for 1 day, 3 days and 10 days, specimens were analyzed by X-ray diffractometry (XRD) and Rutherford backscattering spectroscopy (RBS). It was found that SUS430 specimens formed an oxide layer on the surface. However, it was not clear whether the SiC specimens were corroded or not due to a thick deposit. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

A molten salt mixture of LiF and BeF_2 (which is described as Flibe hereafter) is very attractive as a tritium breeding material in liquid blanket systems of fusion reactors because of its chemical stability and low electrical conductivity. However, Flibe produces TF by neutron irradiation, which is corrosive to structural materials. Thus, the selection of structural materials is a critical issue. It should be done at first based on thermodynamic calculations, and the effect of removing impurities should be demonstrated by experiment. Effects of geometric arrangement and kinetic parameters should be investigated by experiment as well.

There have been some reports about the compatibility of structural materials with Flibe up to the present. A nickel-based alloy was utilized in the molten salt reactor experiment (MSRE) [1]. However, we are interested in Flibe for a liquid blanket system in a fusion reactor such as the force-free helical reactor (FFHR) [2,3]. In this conceptual design, a Ni-containing alloy cannot be accepted because it becomes radioactive with neutron irradiation, but low-activation ferritic steels, vanadium alloys or SiC are considered to be candidates for the blanket structure. Nevertheless, almost no compatiblity data have been obtained.

The corrosion behavior of JLF-1 (Fe–9Cr–2W), V–5Cr–5Ti and SiC, which were candidate structural materials for FFHR blanket systems, was investigated for contact with molten Flibe under neutron irradiation by thermodynamic calculations. It was shown that metal oxides such as Cr_2O_3, Cr_2FeO_4 and VO might be stable in Flibe, and that corrosion by the HF in Flibe might not occur if these oxides formed protective scales on the surface [4]. However, kinetic data on the stability of these oxide layers are required to judge whether they can survive in contact with molten Flibe. In this study, we carried out a preliminary experiment on the corrosion of SUS430 (Fe–18Cr) and SiC in Flibe to investigate compatibility.

2. Experimental

A schematic drawing of the experimental system is shown in Fig. 1. Dipping experiments were performed in

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a stainless steel container with flowing dry argon. In a nickel crucible (10 mm in diameter × 30 mm in depth), each specimen of SUS430 or SiC was dipped for 1 day, 3 days or 10 days in Flibe prepared by mixing LiF and BeF_2 in a ratio of 2 to 1 at 550°C. After the specimen was picked from the Flibe and cooled down, it was cleansed in LiCl–KCl molten salt in order to remove the Flibe solidified on the surface. Then, any LiCl–KCl sticking to the specimen was removed by ultrasonic washing in water, and finally, the surface of the specimen was wiped with alcohol.

Specimens of SUS430 of 0.5 mm × 10 mm × 40 mm were examined as a ferritic steel surrogate instead of JLF-1. Specimens of monolithic SiC (8 mm × 8 mm × 4 mm) were also chosen. The near-surface regions of the specimens were characterized by X-ray diffractometry (XRD) and Rutherford backscattering spectroscopy (RBS).

The XRD analysis was performed using Cu Kα radiation at room temperature. The tube voltage was

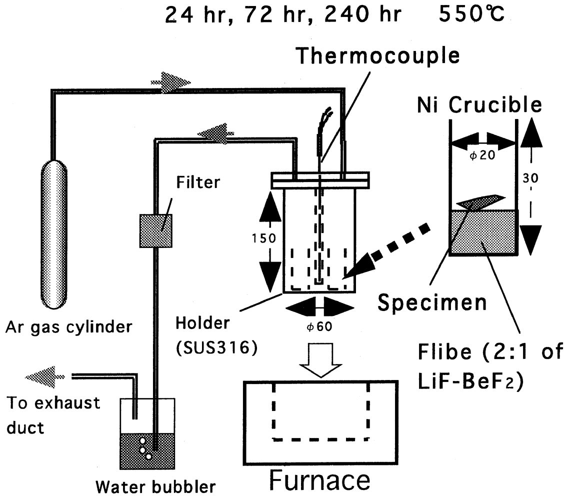

Fig. 1. Experimental system.

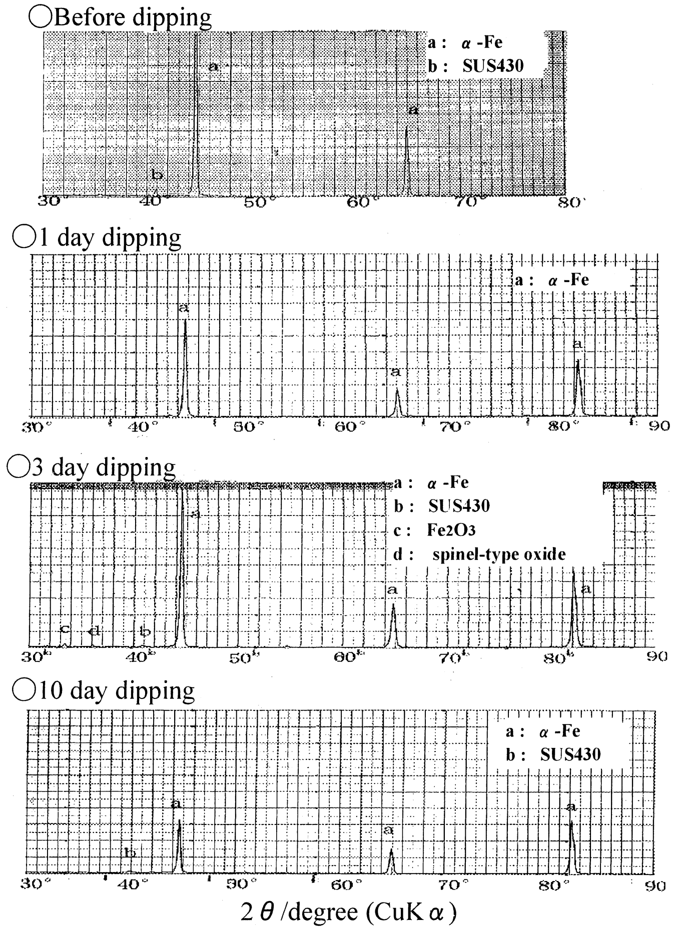

Fig. 2. XRD spectra of SUS430 specimens.

10 kV and the current was 20 mA. This method gives information on the region within a few micrometers of the surface and several tens of mm^2 in area of the specimens.

The RBS analysis was carried out using 3 MeV $^4He^{2+}$ ions (θ_{lab}: 160°) with a tandem accelerator at the Research Center of Nuclear Science and Technology, University of Tokyo. This analysis gives information on the region within several hundred nanometers of the surface. In this analysis, the depth profile is given as the mean value of a region 2 mm in diameter, which is the diameter of the beam. The direct information obtained from the analysis is the mass of the target atoms which made elastic interactions with the projectiles and the energy loss of the projectiles which relates to the depth of the elastic interactions. If the elements existing in the target material are known, the depth profiles of the component elements can be determined.

Generally speaking, the experimentally obtained spectra are compared with those obtained by computer simulation, in which a depth profile is initially assumed. This spectrum simulation is relatively easy, and the basis of this method is described in detail in the literature [5]. Putting the depth profiles of elements in the target material in the computer code RUMP [6,7] gives the energy spectra of projectiles at a prescribed back-scattering angle by calculating elastic scattering and referring to the stopping power [8] of the materials.

3. Results

3.1. SUS430 specimen

Fig. 2 is the XRD pattern of SUS430 specimens after 1 day, 3 days and 10 days of dipping. In this figure, only the peaks assigned to α-Fe were identified in the patterns of the 1 day and 10 day dipped specimens. For the 3 day dipped specimen, on the other hand, small peaks of spinel phases and Fe_2O_3 were observed in addition to the peaks of α-Fe. We suspected that the reason was the non-niformity of the surface of the corrosion product, because those products might come off by washing in LiCl–KCl molten salt.

The RBS spectra after 1 day, 3 days and 10 days of dipping are shown in Fig. 3(a). This figure shows that there are few differences among these three cases. From this figure, the depth profiles of the elements were calculated by the RUMP code.

The element distributions in the 10 day dipped specimens are shown in Fig. 3(b). These depth profiles suggest that oxygen is enriched up to 40 at.% in the near-surface region to form iron and/or chromium oxides. The thickness of the product phase was at most 250 nm. This indicates that the spinel phase cannot be detected by XRD analysis because it is too thin. From the results already mentioned, it is concluded that the normal oxide phases are formed on the ferritic steel surface (e.g., [9,10]), as shown in Fig. 4. It is believed that no destructive corrosion occurs, at least in the initial stage under normal operation condition.

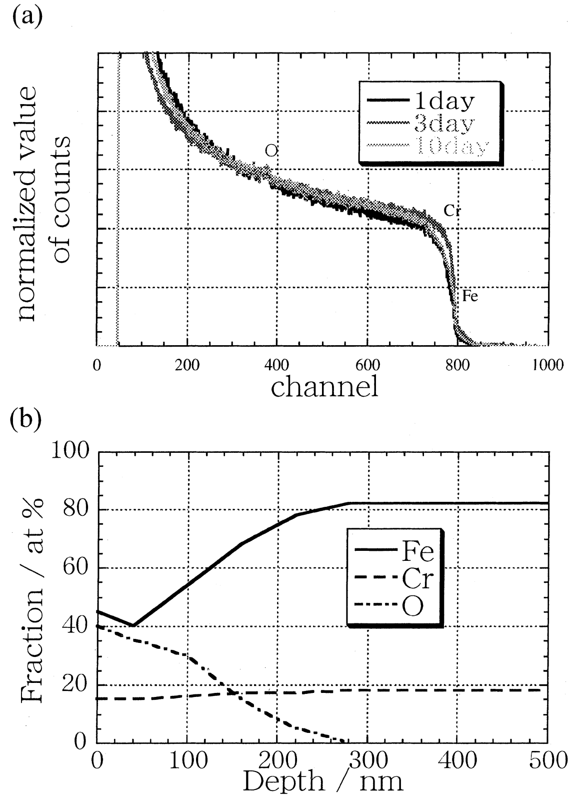

Fig. 3. (a) RBS spectra of SUS430 specimens before and after dipping. The horizontal axis represents the energy of projectiles in 2.8655 keV/channel. The vertical axis shows the backscattering yield in ppm, which is normalized by the total counts. (b) Depth profile of component elements after dipping (SUS430).

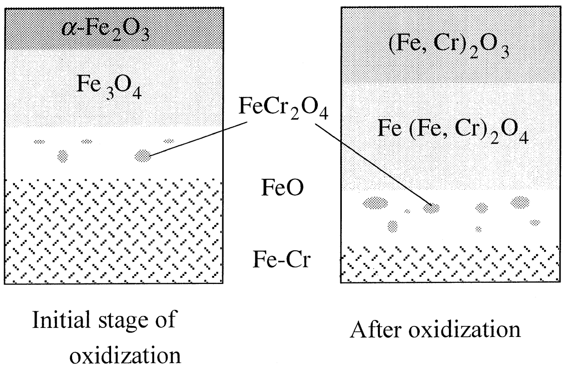

Fig. 4. Model of oxide layer of Fe–Cr alloy.

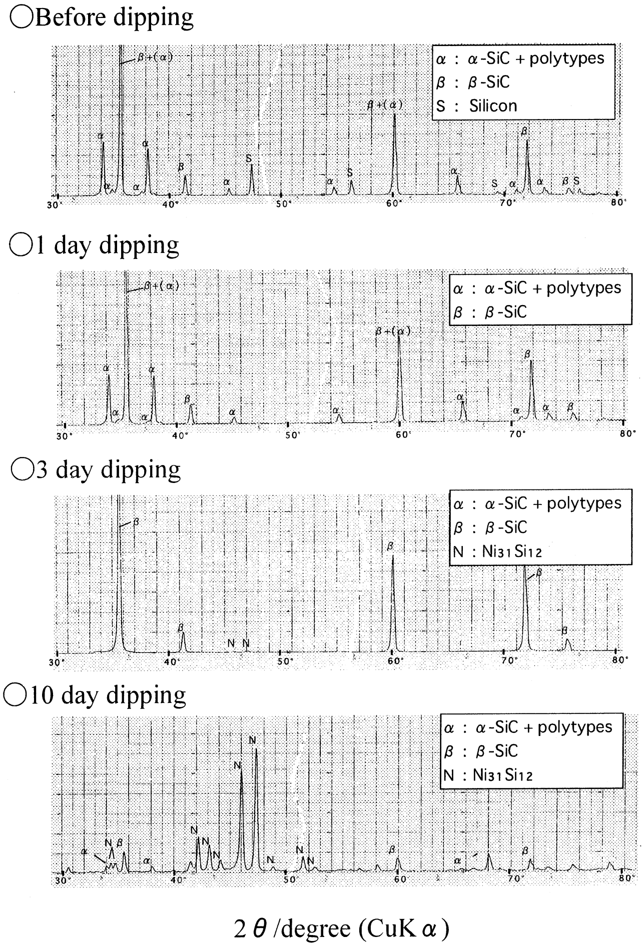

Fig. 5. XRD spectra of SiC specimens.

3.2. SiC specimen

The behavior of SiC specimens was clearly different from that of SUS430. After cleansing the three specimens, black deposits were formed on the surface of the specimens dipped for 3 and 10 days, while only the specimen dipped for 1 day had no deposit.

Fig. 5 shows the XRD patterns of the SiC specimens before and after 1 day, 3 days and 10 days dipping. In this figure, two kinds of XRD-patterns for α-SiC and β-SiC were observed. The peak height of α-SiC decreased with time. For the 10 day dipped specimen, a large number of the peaks assigned to $Ni_{31}Si_{12}$ were detected. On the other hand, only very low peaks of α-SiC were detected. These results suggest that thick $Ni_{31}Si_{12}$ phases were formed on the specimen surface.

Fig. 6(a) shows the RBS spectra of the SiC specimens before and after 1 day, 3 days and 10 days dipping. This figure shows that the chemical composition of the near-surface region was mainly Si, Ni and O.

Fig. 6(b) shows the depth profile of the ratio of Ni in the SiC specimens. It was found that the ratio of Ni concentration near the surface increased with time, and in case of 10 days dipping, the compound layer was more than 2 μm in thickness.

4. Discussion

Though these experiments were carried out in Ar atmosphere, it should be understood that a trace of HF was contained as an impurity because Flibe should have contained HF during the stage of preparation. Water impurity in the system reacts with BeF_2 to produce HF and BeO according to Eq. (1).

$$BeF_2 + H_2O \rightarrow BeO + 2HF. \qquad (1)$$

In fact, a piece of litmus paper set near the outlet of the exhaust became pink. This fact suggests HF evolution

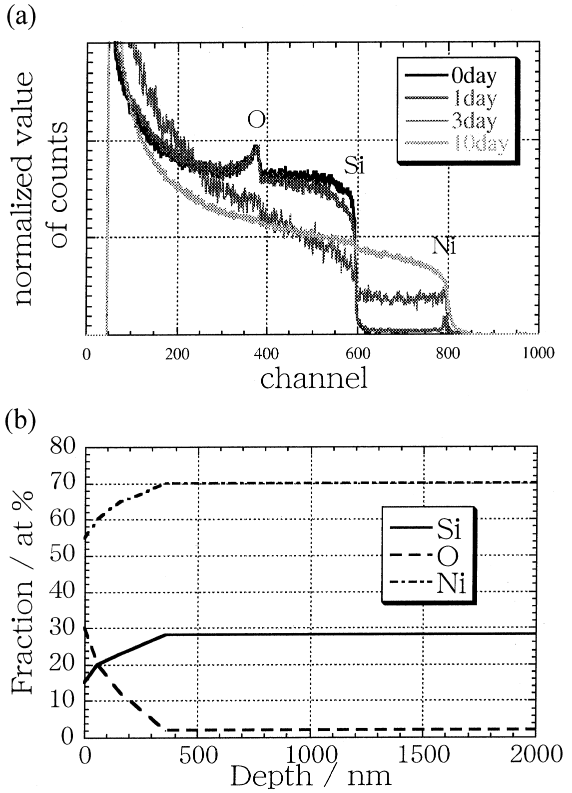

Fig. 6. (a) RBS spectra of SiC specimens before and after dipping. The horizontal and the vertical lines in this figure are the same as those described in Fig. 3(a). (b) Depth profile of component elements after 10 days dipping (SiC).

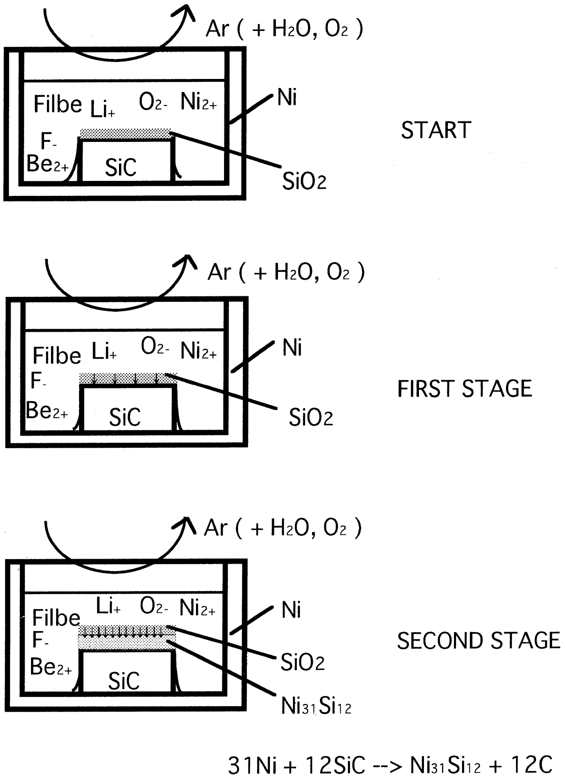

Fig. 7. Possible reaction on the SiC surface.

and the existence of BeO in the Flibe. In this experiment, H_2O is brought into the system as an impurity in Ar.

The compatibility test of structural materials with molten Flibe under TF-containing condition is important because TF is produced due to nuclear reactions in the blanket. In this work, unfortunately, the HF concentration in the system was not measured. In the future, it will be measured and controlled.

The experimental results obtained in this work suggest that ferritic steel might survive with a protective oxide scale in the presence of molten Flibe. For SiC, it is concluded that the $Ni_{31}Si_{12}$ phase grew on the specimen surface with time. Its mechanism can be guessed, as is shown in Fig. 7. At first, Ni atoms penetrate the SiO_2 phase on the surface of the SiC specimens. Secondarily, Ni and SiC react to form $Ni_{31}Si_{12}$ according to

$$31Ni + 12SiC \rightarrow Ni_{31}Si_{12} + 12C. \qquad (2)$$

The thick layer of $Ni_{31}Si_{12}$ formed on the SiC specimens gave no detection of C by RBS for the 10 day dipped specimen. This result also suggests that a kind of stable coating on the surface may work as a protective layer against corrosion in SiC. This phenomenon is very interesting from the viewpoint of in-situ fabrication and self-healing.

In the FFHR blanket design, metallic beryllium pebbles are placed in a Flibe channel as the neutron multiplier, and they are also expected to work as a reducing agent. This function of Be pebbles should also be investigated in the future. Moreover, there are many research topics remaining, including long-time corrosion experiments, for actual structural materials in flowing Flibe under neutron irradiation.

5. Conclusions

Dipping experiments on SUS430 and SiC for 1 day, 3 days and 10 days were carried out under an atmosphere containing a trace of HF at 550°C as a preliminary investigation. The following conclusions were obtained:

1. For SUS430 specimens, no severe corrosion was observed, and a spinel oxide phase was found on the surface. The oxide film may survive in Flibe and work as a protective scale.
2. For SiC specimens, it was not clear whether the specimens were corroded or not due to a thick deposit of

Ni-containing compounds. However, it might work as a protective scale in Flibe.

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