SEM Study of the Chemical Diffusion and Compatibility of D9 Clad with UO₂ Fuel


INTRODUCTION
The structural integrity of the fuel pin is of paramount importance during its stay in a nuclear reactor. The important issues related to high burn-up in sodium-cooled fast reactors (SFRs) are the void swelling and phase stability due to the high fluence of neutron irradiation in addition to chemical diffusion and the compatibility of clad and fuel materials. During reactor operation, the clad and the fuel come in contact after about 40,000 megawatt days per tonne burn-up. Fairly extensive chemical interactions between oxide fuel and clad, in particular, D9, have been reported at high burn-ups which have given rise to premature clad breach. Chemical compatibility of the selected MOX fuel and D9 is an important high burn-up issues in sodium cooled fast reactors. Present studies on chemical diffusion and the compatibility of clad and fuel materials. Interactions and corrosion of structural materials. Her current interests include high burn-up issues of nuclear materials, design and development of new alloys, failure analysis and structural integrity assessment of components using NDE techniques.

RESULTS
Various intermetallic phases formed on the D9 side due to chemical reaction are shown in the SEM micrographs (Figure 1a,b) with the composition of U varying from 15 to 83 %, typical values being shown in Figure 2. The cross-sections of the couples were also analysed. A reaction layer 1-2 µm wide was formed as indicated in Figure 3a,b on the D9 side due to chemical diffusion between the UO₂ and D9 in two sets of specimens heat treated at 823 K for 500 h and 873 K for 312 h respectively. In some regions on the D9 side, the reaction layer had penetrated through the grain boundaries. The twinning observed in the region adjacent to the reaction layer is attributed to strain induced by the product layer. In these specimens, the cross-sections revealed, at some locations, a fairly thick reaction layer approximately 15 µm wide, with a number of porosities or microcavities (image not shown).

In the reaction layer formed in couples treated at 873 K for 100 h, as shown in Figure 4a, a layer about 6-7 µm thick was not in coher-ison with the D9 portion. At some locations, the reaction layer thickness increased up to 25 µm, as shown in Figure 4b.

In couples treated at 973 K for 100 h, a large black patch of reaction product layer was observed on the surface. The cross-section of this specimen showed a uniform reaction layer 12-15 µm wide and at many locations the reaction layer width increased to greater than 30-35 µm, as indicated in Figure 5.

The EDX analysis showed the depletion of Ni in the D9 cross-section (Figure 6). There was some precipitate-like formation on the UO₂ side, as shown in Figure 7a,b, containing Fe, Cr, Ni, etc. The precipitate-like formation seen in Figure 7b is similar to that seen on the D9 side, as shown in Figure 1a,b, indicating cleav-age of such reaction product during separation of the fuel and the clad side of the couple after diffusion annealing treatment.

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Energy-dispersive X-ray spectrometry data from U-rich precipitates on D9 side at 873 K for 312 h.

Strains (5 %) were observed near the hot ends breached at 11 at.% burn-up. Larger cladding pins with similar design operated with D9 clad without breach up to 15 at.% burn-up while PNC 316 clad materials irradiated in EBR II. For second generation MOX fuel pins with D9 et al. [3] have summarized the results of tests made on 6 couples with SS 316 or alloy D9. The results are shown in Table 2. Inter-diffusion studies were carried out with solid-solid diffusion couples assembled with a U-23 at% Zr metal alloy fuel and clad materials such as SS 316, D9 and HT-9. The diffusion couples were annealed at 973 K for four days and examined by light microscopy, SEM and EDX. It was concluded from their work that the structural integrity of the clad material can be maintained for a longer period of time during reactor operation with HT-9 than with SS 316 or alloy D9. The results are shown in Table 2.

Different U-rich and Zr-rich phases of Fe, Cr, and Ni are formed in UO2 couples with SS 316 as well as D9. Phase layers consisting of UFe2 and Zr-rich phases were developed on the clad side of HT-9. With the addition of Pu, the reaction layer is expected to be more for the same O/M ratio of the fuel owing to enhanced inter-diffusion [5]. From the systematic inter-diffusion studies of fuel-clad compatibility in IFR by Keiser et al. [5], it can be concluded that Pu is the highly diffusing clad constituent while U and Pu are the diffusing fuel constituents. Compared to the diffusion observed in U-Zr binary metallic fuel, the addition of Pu greatly enhanced the extent of diffusion and affected the types of phases observed. Keiser et al. have also concluded [6] that Pu increases the inter-diffusion of various components in fuel-clad diffusion couples. This effect of Pu can be assumed to be pronounced in oxide system also. The enhanced precipitation on the D9 side is attributed to the vacancy wind effect [7-9]. When there is a large difference in the diffusivity of constituent elements in diffusion couples, as in the D9-UO2 system, excess vacancy concentrations are produced on the D9 side, which give rise to precipitation.

In the D9-UO2 system, the diffusion of elements such as Fe, Cr, Ni, etc. into the UO2 side is comparatively much higher than that of U into the D9 side. With the advent of metallic fuels for future FBR applications, multicomponent diffusion assumes greater importance to understand the diffusion behavior of metallic fuel and clad, when they come in contact after certain burn-up (about 2-3 at% burn-up).

According to Manning [10], the diffusion coefficients in a multicomponent system can be represented by an n2 matrix. Suppose there are three elements in the fuel side and four elements in the clad side, it can be represented by an n2 matrix. Suppose there are three elements in the fuel side and four elements in the clad side.
major elements in the clad side, then a seven by seven diffusivity matrix can explain the diffusion behavior. When $D_{ij} = D_{ji}$ (off-diagonal terms), microscopic reversibility principles are valid that lead to smooth composition profiles and no intermetallic phase formation. Intermetallic phase formation would lead to fluctuations in the composition profiles. The diagonal terms of the matrix are self-diffusion coefficients and off-diagonal terms are impurity diffusion coefficients. Multicomponent diffusion, the vacancy wind effect and the diffusivity matrix are discussed in detail elsewhere [11,12]. The results described here clearly indicate strong interactions, the formation of intermetallic phases, and there is no possibility of smooth composition profiles in a UO$_2$-D9 system.

CONCLUSIONS
In mixed oxide fuel, when fuel and clad come into contact, strength reducing diffusion zones, oxide layers, etc., are formed. Prolonged contact of fuel and clad would affect the structural integrity of the clad. Preliminary experiments of chemical diffusion and the compatibility of UO$_2$ and D9 carried out in the present study strongly points to this. Factors such as U-rich particles formed in proximity to grain boundaries, a chemical reaction layer 15-µm wide consisting of numerous porosities, cavities, etc. (for the relatively short duration of contact at 873 K) act against the structural integrity of the clad. At certain locations, the reaction layer thickness increases to 25 µm in couples annealed at 873 K for 1000 h. In specimens heat treated at 973 K for 100 h, the reaction layer at many locations increases beyond 35 to 40 µm.

Under actual reactor operating conditions, with the added effect of MOX fuel, irradiation damage, fission products and their interaction, depleted layer formation due to sodium coolant flow on the other side, etc., the interaction scenario could become more complicated. It is thus important to generate data on the chemical compatibility of the selected MOX fuel with D9 and other candidate clad materials.

REFERENCES

**Table 1:** Chemical composition of alloy D9 (wt%)

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>S</th>
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<td>0.505</td>
<td>1.509</td>
<td>15.068</td>
<td>15.051</td>
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<td>Ti</td>
<td>Ta+Nb</td>
<td>N</td>
<td>B</td>
<td>Fe</td>
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<td>0.315</td>
<td>0.020</td>
<td>0.007</td>
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**Table 2:** Fuel-clad chemical interaction (FCCI) in U-Zr fuel system with selected clad materials [1].

<table>
<thead>
<tr>
<th>Fuel: U, 23 at% Zr</th>
<th>Clad: HT-9</th>
<th>Reaction layer (µm)</th>
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<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
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