To be fully effective, the cladding encapsulating nuclear fuel must be highly resistant to radiation damage, be relatively transparent to thermal neutrons, have effective corrosion resistance and good mechanical properties.

Zirconium alloys are well suited to these needs and have therefore to date been the most favoured material for fuel cladding. Commonly used alloys such as Zircaloy-2, Zircaloy-4, M5TM and ZIRLOTM also include small amounts of iron which has been shown to increase corrosion resistance.
The Challenge

In order to fully understand the long-term effectiveness of these materials, scientists needed to understand the mechanisms by which iron effects the oxidation and hydrogen pick up rate of thermally grown zirconium alloys. They also required further insights into the defect concentrations.

The Solution

Scientists at Imperial College performed DFT (computer modelling) to predict the effect of alloying with Fe on the oxidation of Zr alloys.

Scientists at the National Nuclear Laboratory then applied a combination of XRF and Zr & Fe K-edge XANES on I18 at Diamond to identify the zirconium and iron distribution, along with the chemical speciation in the oxide film on Zircaloy-4 fuel cladding material.

They examined the oxidation state of the Fe near the metal-oxide interface and near the oxide outer surface. Through chemical mapping, they were able to demonstrate that the ratio of Fe²⁺ to Fe³⁺ did indeed change across the oxide, confirming the DFT predictions. They were also able to show that metallic Fe was retained many microns from the oxide-metal interface, showing that equilibrium was not immediately attained. The kinetic delay in oxidation was attributed to the inhomogeneous distribution (precipitation) of Fe in the metal matrix.

The Benefits

The results of the research clarify how Fe additions to Zr alloys can, via the equilibrium role of Fe ions in the oxide, reduce corrosion rates and hydrogen pickup. They also show that, in practice, the equilibrium state is not immediately achieved, indicating that thermo-mechanical treatments affecting the distribution of Fe-rich precipitates in the metal could increase the benefits achieved by alloying with Fe. The insight gained from this study will have a fundamental impact on the development of fuel cladding in the future, increasing fuel efficiency while retaining or improving reactor safety.

“In order to investigate the oxidation states of Fe – an alloying element important for Zircaloy nuclear fuel cladding in terms of corrosion resistance – we were recommended to use the XANES technique combined with the specialised micro-sized beam available on I18. The success of this initial experiment and the brilliant support of Diamond staff was key to NNL performing further experiments at Diamond on other beamlines, in the knowledge that we would be exceptionally supported throughout.” Dr Helen Swan, Senior Research Technologist (Materials Science), Materials and Reactor Chemistry, National Nuclear Laboratory

For further information

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