Chemical compatibility between U-6wt.%Zr alloy and T91 cladding

Santu Kaity, T.R.G. Kutty and Arun Kumar
Radiometallurgy Division
and
Renu Agarwal
Product Development Division
and
A. Laik
Materials Science Division
and
H.S. Kamath
Nuclear Fuels Group, BARC

This paper received the Best Poster Award at the 9th International Symposium on Materials Chemistry (ISMC 2010), held at BARC, Mumbai, during December 7-11, 2010

Abstract
Fuel-Clad Chemical Interaction (FCCI) is recognized as one of the major concerns for metallic fuels because of formation of low melting eutectic. The measured eutectic temperature between U-6wt.%Zr alloy and T91 steel was found to be almost similar to that of U-Fe system, i.e. 722ºC. Addition of 6wt.% Zr in uranium and presence of alloying elements of T91 steel i.e. Cr, Mo, V, Nb etc. will not have significant effect on eutectic temperature. The interdiffusion between U-6wt.%Zr and T91 at 700°C resulted in formation of (U,Zr)(Fe,Cr)₂, Zr-rich and Zr-depleted layers at the interface, whereas at 750°C, reaction between these two caused eutectic melting and resulted in the formation of U₆Fe, U(Fe,Cr)₂ and Zr(Fe,Cr)₂ phases.

Introduction
Metallic fuel is considered for future Fast Breeder Reactors (FBRs), due to its high breeding potential, high thermal conductivity, high fissile and fertile atom densities, low doubling time and ease of fabrication as compared to other ceramic fuels. However, a few shortcomings of metallic fuels such as, low solidus temperature, high swelling rate and susceptibility to chemical and mechanical interaction with cladding materials, prevent them from achieving their full potential. Primarily, two design concepts have been proposed for the metallic fuel development programme for FBRs in India. One of them is based on sodium bonded ternary U-15Pu-6Zr (composition in wt.%) alloy with T91 grade steel clad, and the other consists of binary U-15Pu alloy, mechanically bonded to T91 clad with a Zr liner between the fuel and clad. The schematic diagrams of cross-sections of conceptual fuel pin design, are shown in Fig. 1. Uranium, U-6Zr alloy are the proposed blanket materials. T91 cladding material is a 9Cr-1MoVNb steel, having ferritic-martensitic structure. In contrast to austenitic alloy steels, ferritic steels have the advantage of greater resistance to void swelling. T91 steel exhibits high mechanical strength,
and combines low thermal expansion with high heat conductivity\textsuperscript{3}.

The chemical compatibility between fuel and clad material also known as Fuel-Clad Chemical Interaction (FCCI) is of prime importance, because of formation of low melting eutectic, which may sometime limit the life of the fuel pin, in a reactor. In the present investigation, chemical compatibility between U-6Zr alloy and T91 cladding has been studied, by measuring eutectic temperature by Differential Scanning Calorimeter (DSC), followed by diffusion couple experiments at 700°C and 750°C for heating upto 500 hrs.

**Experimental**

The purities of starting materials, uranium and zirconium, were 99.9% and 99.95%, respectively. U-6Zr alloy samples were prepared by following injection casting route. T91 grade steel was supplied by Larsen & Toubro. The heat treatment for T91 consists of austenization at 1050°C and air quenching followed by tempering at 750°C for 1 h.

**Eutectic reaction measurement between U-6Zr and T91**

For measuring the eutectic reaction temperature between U-6Zr and T91, U-Zr-T91 alloy (having 82 wt.% U, 5 wt.% Zr) was prepared by arc melting of U-6wt.%Zr and T91, in a highly purified helium atmosphere, on a water-cooled copper hearth. U-Fe alloy was (having 90 wt.% U) was also prepared to compare with the U-Zr-T91 alloy. The alloy samples were further heated at 700°C in high purity argon atmosphere, to obtain perfect homogeneity. The eutectic temperature measurements were carried out, using a heat flux type Differential Scanning Calorimeter (DSC). The heating and cooling rates were programmed at 1 K/min. After the melting experiment, the microstructures of the polished samples were examined by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscope (EDS).

**Diffusion couple experiment between U-6Zr and T91**

U-6Zr alloy and T91 steel were cut into small discs and then the surfaces of all these discs were polished using 1 μm diamond paste. The diffusion behaviour between U-6Zr and T91 was studied by diffusion couple experiment of U-6Zr/T91, where a disc of U-6Zr alloy was sandwiched between two discs of T91. These ‘sandwiches’ were kept inside a fixture made of Inconel 600 alloy. Ta foil was used to prevent any reaction between samples and fixture. The fixtures containing these samples were encapsulated in quartz tube under helium gas. The diffusion couples were annealed in a resistance heating furnace maintained at 700 and 750°C for up to 500 h. Subsequent to annealing, the couples were sectioned using a slow speed diamond cutting wheel. The exposed cross sections were polished to 1 μm surface finish. The extent of reaction and phases formed at the interface were analyzed by SEM/EDS. Further microstructural characterization was carried out using CAMECA SX-100 Electron Probe Micro-Analyzer (EPMA) equipped with Wavelength Dispersive Spectrometer (WDS).

**Results and Discussion**

**Eutectic temperature**

The DSC curves for different alloy compositions are shown in Fig. 2 indicating the eutectic reaction temperatures. The measured eutectic temperature between U-6Zr alloy and T91 was found to be 722°C, which is almost equal to that of U-Fe system. The results indicated that fuel-clad eutectic temperature was not changed with the addition of 6wt.% Zr in the fuel. Similarly, alloying elements of T91 grade steel i.e. Cr, Mo, V, Nb etc. have no
remarkable effect on the eutectic temperature. These results concluded that the main contributors to the fuel-clad eutectic reaction are U of the fuel and Fe of the cladding. U-Fe alloy has the lamellar microstructure of U₆Fe (bright phase) and UFe₂ (dark phase) as shown in the Back Scattered Electron (BSE) micrograph (Fig. 3a). The BSE image as shown in Fig. 3b reveals that the microstructure of U-Zr-T91 system is much different from the layered structure, as observed in case of U-Fe system.

The BSE image shows that three phases are formed in the alloy: bright matrix phase (U₆Fe), grey (U(Fe,Cr)₂) and a dark phase (Zr(Fe,Cr)₂). Zr has limited solubility in U(Fe,Cr)₂ and U has limited solubility in Zr(Fe,Cr)₂.

**Diffusion behavior of U-6Zr and T91**

Figs. 4(a-b) show the SEM micrographs of the reaction layer formed at the interface between U-6Zr and T91 after annealing at 700°C for 500 h. The intensity profile of U-M₅α, Zr-Lα, Fe-Kα, Cr-Kα x-ray lines recorded across the interface, along the line AB is shown in Fig. 4(c). The interdiffusion between the two specimens resulted in the formation of three different layers at the interface: a diffusion reaction layer of thickness around 10 µm, a thin Zr-rich layer of thickness 2-3 µm and a Zr depleted layer of 15-20 µm. The formation of such diffusion layer can
easily be explained with the help of the mechanism given by Hofman et al.1. Zr diffuses out of U-2Zr alloy due to its affinity for nitrogen on the surface. Due to the sluggish nature of diffusion reaction between Zr and Fe4, this Zr cannot react with T91 steel. Thus there is a Zr rich layer (layer B, Fig. 4b) on the surface and a Zr depleted inner zone (layer C) to maintain mass balance of Zr element. However, due to strong interaction of U with Fe of T91 steel, some uranium diffuses through this Zr-rich layer and comes in contact with Fe of the steel. This results in formation of a U-Fe layer (layer A) closer to T91 and outside Zr-rich layer. This outermost layer (layer A) has small amount of Cr and Zr, forming (U,Zr)(Fe,Cr)2 with — 10 at.% Zr and — 5 at.% Cr. The Zr rich layer acts as a barrier, by reducing the penetration of Fe and Cr elements through it towards fuel lattice. Therefore, amount of Fe and Cr in layer C are negligible.

When the annealing temperature was increased to 750°C, eutectic-melted microstructure was observed as shown in Fig. 5 and they were much different from the layered structures formed below the eutectic temperature. The bright phase was identified by EDS as U6Fe, the grey and dark phases are U(Fe,Cr)2 and Zr(Fe,Cr)2, respectively. The results indicate that the measured eutectic temperature between U-6Zr and T91, is very crucial from reactor safety point of view. In any case, if the clad temperature reaches above the eutectic temperature, the direct contact of U-6Zr and T91 cladding would cause eutectic melting, as observed in this diffusion couple experiment.

References

Fig. 5: BSE micrograph of the diffusion couple U-6Zr/T91 annealed at 750°C for 100 h.