Phase distribution study for U-Zr-metallic simfuel

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A detailed study of the phase evolution in a U-10 wt% Zr alloy fuel simulated with fission products corresponding to 10 atom% burn-up and annealed at 700°C and 1000°C in vacuum is carried out by using XRD and microscopic techniques like SEM and EDS. The studies revealed segregation of major phases like bcc-U, U and U-Zr. SEM studies revealed the presence of segregated phases in the bulk matrix of uranium. Salient results are presented in this article.

1. Introduction

Nuclear power is an alternative currently available to supply enough energy to bring down global CO₂ level and this would require efficient harnessing of nuclear resources. The inception of nuclear technology took place with an all-metal fuel concept with liquid metal coolant reactors (LMRs) [1], obviously for the advantages like well-known chemical and physical behavior of metals and their alloys, ease of fabrication, simpler and smaller core designs, production of artificial fissile (239 Pu/233 Th) material inventory along with excellent neutron economy, high burn-up capability with inherent safety features and straightforward recycling by techniques like electro-refining. The emergence of the concept of integral fast reactor (IFR) is consociated with the recognition that the 238 U reserve of world must be efficiently utilized as an energy source in the centuries to come. Thus, the fuel system must be able to utilize plutonium as its principal fuel and must have the potential to simultaneously create 238 Plutonium by breeding 239 U. However, the low melting temperatures of pure plutonium and pure uranium-plutonium alloys makes it impractical to design a commercially viable reactor using only these elements. Several elements like Cr, Mo, Ti and Zr have been considered as additives for increasing the melting temperature. Out of these elements Zr is unique, since it enhances the compatibility of fuel and SS clad by suppressing the interdiffusion between them. By the end of 1960s, 10 wt% of zirconium and 20 wt % of plutonium alloy fuel (remaining uranium) with satisfactory fuel-clad compatibility and raised solidus temperature had been developed.

The appropriate selection of alloy fuel is closely linked with their metallurgical characteristics along with other thermo-physical and neutronic characteristics. The metallurgical properties of alloy fuel systems, like the binary alloys of plutonium and zirconium with uranium as base matrix have been extensively studied. U-Zr binary alloy is an important sub-system of the U-Pu-Zr ternary alloy which provides alternate choices of alloy fuels. U-rich Zr alloys are known to exhibit excellent corrosion resistance and dimensional stability during thermal cycling. Based on irradiation experiments, the alloy U-10 wt% Zr has been proposed as a prospective fuel for fast breeder reactors [2]. A number of reports are available in literature on properties of Zr-rich U-Zr alloys [3, 4] and U-rich U-Zr alloys [5-7]. Broadly, these studies indicate the formation of saturated alpha-U type phase in U rich region while gamma (bcc) or hexagonal (h) type phase in Zr rich regions. Also, it has been observed that hexagonal (h) UZr, type phase precipitates on annealing the alloys.

Based on the literature information, it can be concluded that the virgin fuel itself can give rise to a wide variety of microstructures depending on composition and thermal history. Moreover, the porosity and microstructure of U-Zr alloy are strongly dependent on the composition and phases of the alloy. The porosity also influences the extent of fuel swelling and gas release which affects the integrity and performance of fuel. Thus it is desirous to know the phase evolution of a fuel subjected to a sufficiently high burn-up. Such fuel contains myriads of fission products along with alloying elements. This situation generates several phase fields due to interaction of base matrix elements and fission products and this leads to phase segregation induced structural changes in the microstructure of fuel assembly. Reported information shows successful performance of alloy fuel with the porous matrix in achieving 10-15 atom % burn-up [8]. With an aim to generate
information on phase and micro-structural changes in high burn up conditions, a detailed study of the phase evolution in a U-10wt%Zr alloy fuel simulated with fission products corresponding to 10 atom% burn-up and annealed at 700° and 1000°C in vacuum is carried out by using XRD and microscopic techniques like SEM and EDS. The salient results are presented in this article.

2. Experimental

U-rich U-Zr alloys (U-10 wt%Zr) were prepared by melting appropriate amounts of elements in an arc melting furnace in an inert (Ar) atmosphere. Oxygen impurity in the flowing Ar gas was removed by passing it over hot uranium turnings. The alloy buttons thus obtained were re-melted 3-4 times to ensure chemical homogeneity. Prior to incorporation of the noble metal fission products (Pd, Ru, Rh, Mo) in the parent alloy button they were reduced in 8%H2-Ar at 700°C for 3 h to remove any oxide impurity present. After this treatment, calculated amounts of Pd, in form of small wire pieces, and Ru, Rh and Mo as powders (obtained from integrated fission product yields of natural uranium corresponding to 10 atom% burn-up) were added to the parent alloy button and melted in arc melting furnace several times for homogenization. To a portion of this simulated alloy calculated amounts of Nd and Ce pieces (preserved in oil) were added and re-melted in arc melting furnace. The schematic of preparation of alloys of various compositions and their annealing protocol are shown in Fig. 1. The composition of the alloy with respect to the incorporated fission products (g/10g of natural U) is: Ru (0.9257), Rh (0.2551), Pd (0.5544), Mo (0.8667), Nd (0.9851), Ce (0.7418).

For the micrographic and XRD studies the alloys were cut into small pieces using slow speed diamond coated cut-off wheel. Standard metallographic procedures were followed for grinding and polishing. A small piece of the alloy was electro leached using aqueous solution of 50% H3PO4 as electrolyte and SS304 as cathode with a standard potential of 2 V. Micrographic characterizations were carried out using scanning electron microscope (SEM). The compositional analyses were carried out by energy dispersive spectroscopy (EDS). The same set of experiments was carried out at 1000°C with a separate set of alloys.

3. Characterization of phases

3.1. XRD studies

Initially all the XRD patterns were compared with the known phases of U and other compound phases (Fig. 2). The identification of phases from their corresponding XRD patterns were carried out by considering structure types known for different phases of U alloys. Since exposure area of sample in diffraction experiments is 0.5 x0.5 mm, they provide the average existing bulk information. The change in focus spot on sample did not reveal any significant change in the diffraction patterns. Thus only the major phases could be identified by the XRD studies. The details of analyses of different samples are explained below.

The XRD pattern of the as cast alloy shown in Figure 2 indicates significantly broadened Bragg peaks. The analyses of the peaks were carried out by comparing the reported standard XRD patterns of known alloys or elements used as constituents. The absence of alpha-U can be ascertained in all the samples as can be seen from Fig. 2. It needs to be mentioned here that the XRD peaks cannot be simply assigned to the known phase, due to the usage of diverse elements. Thus the analyses were carried out by considering various lattice types and typical unit cell parameters of the assigned phases. From the positions of intense peaks, two distinct stabilized bcc phases with unit cell parameters a = 3.40 and 3.33 Å could be suggested for sample E (Fig. 3a). Both position and intensity of the intense peaks can be accounted by these two bcc phases. In addition, a monoclinic U,Ru type ([JCPDS-PDF 18-1145] and a tetragonal (β-U) [10] phase could also be
identified from the observed peaks. Most of the observed peaks in XRD pattern could be explained by considering these four phases.

No hexagonal δ phase (UZr₂) phase [12] could be observed in this XRD pattern. As mentioned, each of the stabilized bcc phases of U may have some solubility of the added elements. The stabilization of bcc phases with Mo, Ru and Zr etc elements is known for uranium. Further the peak positions attributed to U₃Ru type phase and β-U phase are also not strictly matching with their reported unit cell details. Thus solubility of some added elements in these lattices also cannot be ruled out. No clear identification for the noble metals could be ascertained from this XRD pattern, which may be due to their insignificant contribution in the exposed area in XRD experiments or masking by the dominating peak of U-containing phases.

XRD patterns of sample A and D, the lower temperature (700°C) annealed U-Zr alloy containing noble metals and U-Zr alloy containing noble metals and rare-earth elements respectively, shown in Fig. 4a and 4b, are distinct from all other samples. In the sample D, the presence of bcc U phase (a = 3.41 Å) is clearly observed in the XRD pattern (Fig 4b). However, the presence of monoclinic U₃Ru type phase may also be suggested from the peak position at 34.8° and 41.5°. A closer analysis of the peak at 37.2° indicates splitting, which might be due to composition heterogeneity of the bcc phase of U. Considering the multiplets of the 37.2° peak, this sample may have total three types of cubic phases, with unit cell parameters as: 3.43, 3.41 and 3.26 Å, respectively. Similar analyses of the XRD pattern of Sample-A (Fig 4a) revealed the presence of two types of bcc-U phases (a = 3.40 and 3.39 Å). The appearance of peaks at 34.8° and 41.5° suggests the presence of U₃Ru type monoclinic phase. However most of the peaks expected for U₃Ru type monoclinic phase are not observed. Some of the peaks could be attributed to -U and a feeble amount of fluorite type UO₂ phase can also be guessed from the broad peak at 28.1° (JCPDS-PDF 78-0725)

A simple comparison of the XRD patterns (Fig 4d and 4c) of high temperature annealed (1000°C) alloys, namely sample B (U-Zr alloy containing noble metals and rare-earth elements) and sample-C (U-Zr alloy containing noble metals) indicates
some similarity. In both the XRD patterns the bcc phase of U could be identified. In contrast to sample-B, where two types of stabilized bcc phases exist, the sample C shows only one type of bcc phase. The peaks attributable to bcc phase in sample B could be assigned to \(a = 3.46\) and \(a = 3.32\) Å, while the identified bcc phase in sample C has unit cell parameter: \(a = 3.44\) Å. This difference can be due to redistribution of elements at higher temperature. The unit cell parameters observed for sample C might be due to incorporation of elements of wider atomic radii.

It may also be important to note that broad overlapping peak like features are observed at the positions of -U (Cmcm), [11] in sample B (inset in Fig. 4d). However no clear information can be obtained due to poor peak shapes in this XRD pattern. Further it can be noticed that in both sample B and C, U,Ru type monoclinic phase is observed. Thus the sample C has only one stabilized bcc phase which probably disintegrates in sample B, due to additional constituent elements (such as Nd and Ce). The observed U,Ru type phase does not show much difference in these two XRD patterns. The segregation of elements may be a reason for the appearance of the -U phase. Also, a broad hump or peak observed at two-theta ~ 29° in the XRD pattern of both B and C may be due to surface oxidation of uranium metal to fluorite type UO\(_2\) phase (JCPDS-PDF 78-0725).

3.2. Contrast and microstructure studies by SEM-EDS.

The SEM micrograph of sample E (as-cast alloy of U-Zr containing noble metals) shows almost uniform microstructure with different contrast indicating the presence of one each of U-rich Zr deficient and U-deficient-Zr-rich phases (Fig. 3b, Table 1). This is different from the fine lamellar structure present in U-10wt%Zr as-cast alloy with a single phase as reported in literature [13]. This observation is in accordance with the XRD results. Though the microstructure appears close to that reported for UZr\(_2\) type phase [12], the absence of corresponding peaks in the XRD pattern (Fig. 3a) excludes its existence. No distinct contrast for -U and U\(_2\)Ru, as identified by XRD, is seen in the SEM micrograph.

Table 1: EDS analyses results (as atom fraction) of U-Zr + Noble metals as-cast alloy

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom Fraction</th>
<th>Element</th>
<th>Atom Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.08</td>
<td>U</td>
<td>0.52</td>
</tr>
<tr>
<td>Zr</td>
<td>0.5</td>
<td>Zr</td>
<td>0.04</td>
</tr>
<tr>
<td>Ru</td>
<td>0.14</td>
<td>Ru</td>
<td>0.08</td>
</tr>
<tr>
<td>Rh</td>
<td>0.04</td>
<td>Rh</td>
<td>0.008</td>
</tr>
<tr>
<td>Pd</td>
<td>0.16</td>
<td>Pd</td>
<td>0.04</td>
</tr>
<tr>
<td>Mo</td>
<td>0.06</td>
<td>Mo</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Fig. 4: XRD patterns of sample-A (a), sample-D (b), sample-C (c), sample-B (d)
The sample A, which is obtained by annealing the alloy containing noble metals at 700 °C shows segregation of different phases with different contrast like white, light grey and dark regions (Fig-5a). The EDS analyses (Table 2) on the light phase show that it is U rich, Zr deficient with no Pd. The other two phases contain all the noble metals along with the parent components. The dark grey phase is richer in Pd and Mo than the lighter grey one. However, this noble metal containing phases could not be seen in XRD. The SEM micrograph of the sample C which is obtaining by annealing the alloy at 1000 °C shows two phase fields (Fig 5b). The original dark grey phase of the original alloy remains unchanged in their elemental composition during annealing at 1000°C. However, the white and light grey phases observed at low temperature annealing appear to merge into a grey phase with needle shaped morphology. This phase is rich in Rh and Pd but deficient in Mo when compared to the corresponding phases in 700°C annealed sample (Table 2). The observed two phase type behavior indicates the presence of dark grey bcc-U phase and lighter grey U,Ru type phase containing the Rh and Pd etc.

On addition of rare-earths elements, the distinct transformation of the microstructure of as-cast alloy into dark patches with intricate network structure and lighter region with four different phases having slightly varying contrasts is observed (Fig. 5f, Table 3). Significant changes are observed on annealing this alloy sample. The 700 °C annealed sample (sample D, Fig. 5c) shows two sharply contrasting regions: Dark patches and lighter regions having isolated phase precipitations. The dark patches are Pd, Nd and Ce rich.

### Table 2: EDS analyses results (as atom fraction) of U-Zr+Noble metals annealed alloys.

<table>
<thead>
<tr>
<th>Elements</th>
<th>UZr matrix + Noble metals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700°C annealed</td>
</tr>
<tr>
<td></td>
<td>White region</td>
</tr>
<tr>
<td>U</td>
<td>0.73</td>
</tr>
<tr>
<td>Zr</td>
<td>0.017</td>
</tr>
<tr>
<td>Ru</td>
<td>0.02</td>
</tr>
<tr>
<td>Rh</td>
<td>0.009</td>
</tr>
<tr>
<td>Pd</td>
<td>0.0</td>
</tr>
<tr>
<td>Mo</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Elements U Zr Ru Rh Pd Mo Nd Ce

White matrix Interconnected dark region Isolated dark spots

Table 3: EDS analyses results (as atom fraction) of as-cast U-Zr + Noble metals + Rare-earth elements alloy

Table 4: EDS analyses results (as atom fraction) of (U-Zr + Noble metals + Rare earth elements) alloy annealed at 700°C.

Table 5: EDS analyses results (as atom fraction) of (U-Zr + Noble metals + Rare earth elements) alloy annealed at 1000°C.

Elements U Zr Ru Rh Pd Mo Nd Ce

Table 3: EDS analyses results (as atom fraction) of as-cast U-Zr + Noble metals + Rare-earth elements alloy

Table 4: EDS analyses results (as atom fraction) of (U-Zr + Noble metals + Rare earth elements) alloy annealed at 700°C.

Table 5: EDS analyses results (as atom fraction) of (U-Zr + Noble metals + Rare earth elements) alloy annealed at 1000°C.

(Table 4) and have platelet-like microstructures in the as-cast samples (Fig.5f). They get transformed to network like microstructure when annealed at 700°C (Fig. 5d). The lighter region is a homogeneous distribution of four phases with varying proportions of the component elements as follows:

a) White region which is highly U-rich and moderately Mo-rich.

b) Light grey region which is U and Ru-rich with moderate amounts of Zr.

c) Grey region which is Zr and Ru rich with moderate amount of U.

d) Highly Pd and Rh rich grey spots. The XRD analyses of this sample showed presence of U,Ru and bcc-U type phases.

The contrast variations might be due to different extent of substitution of other elements in both bcc and U,Ru phases. On annealing this alloy to 1000°C (sample B) the alloy gets restructured to three phases (Fig. 5e): A white U-rich region with moderate amounts of Ru, Mo and Zr, a Ru-rich grey region and Pd-rich grey spot-like phase precipitates containing moderate amounts of Rh, Ru and the rare-earths (Table 5), although XRD analyses indicates the presence of five phases. The reason for obtaining lower number of phase contrasts from micrographic analysis might be different pattern of distribution of noble metals and rare-earth elements into the basic lattices.
4. Conclusion:
Phase distribution studies were carried out on U-10wt%Zr
alloy simfuel using XRD and micrographic (SEM-EDS)
techniques. The salient phase features of the annealed simfuel
alloys deduced from these studies are as follows:
i) U-Zr alloy containing noble metals and annealed at
700°C contain two bcc phases while the alloy with noble
metals and rare-earth elements and annealed at 700°C
contain three bcc phases. On annealing these respective
alloys to 1000°C the number of bcc phases get reduced to
one and two, respectively. The observation of multiple bcc
phases may be due to substitution of different elements to
different extents leading to composition heterogeneity.

ii) All the annealed alloys show the presence of monoclinic
U,Ru phase with dissolved noble metal or rare-earth
elements in it.

iii) Alloy containing only noble metals show the presence of
additional phase like less-symmetric -U while the alloy
with noble metals and rare-earth elements (1000 °C
annealed) show the features similar to -U.

iv) All the features observed in XRD of both as-cast and
annealed samples are not observed in SEM and vice versa.
This is probably due to lot of dissolution and re-
distribution of noble metals and rare-earth elements
amongst the main parent lattices.

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