Thermal properties of (Al,Gd)O$_3$ doped uranium dioxide

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Abstract. In this paper were defined thermal characteristics (thermal diffusivity up to 2000 °C, heat capacity up to 1250 °C and thermal conductivity of up to 1250 °C) of oxide nuclear fuel with additives of burnable neutron absorber in the form of (Al,Gd)O$_3$. Also for comparison samples UO$_2$ with gadolinium Gd$_2$O$_3$ and pure uranium dioxide were studied. It is shown that the thermal diffusivity and thermal conductivity of UO$_2$ with dopant of gadolinium in the form of (Al,Gd)O$_3$ is considerably higher than those of Gd$_2$O$_3$–doped uranium dioxide, due to the fact that (Al, Gd)O$_3$ does not form a solid solution with UO$_2$.

1. Introduction
In order to achieve high burnup of WWER fuel requires using burnable neutron absorbers (Gd for WWER fuel), to reduce the reactivity in the initial stages of TVEL action. But the injection to the fuel gadolinium in the form of Gd$_2$O$_3$ leads to a significant reduction of uranium dioxide thermal conductivity [1,2,3], and as a consequence an increase of the temperature gradient between fuel and cladding. To solve this problem were offer to inject in uranium dioxide gadolinium as a perovskite phase AlGdO$_3$, which improves the thermal conductivity of the fuel without sacrificing Gd amount in it [4].

To carry out the work following uranium dioxide samples were made: R - pure uranium dioxide, G - uranium dioxide with 6.9% Gd$_2$O$_3$ and AG - uranium dioxide with 8.9% AlGdO$_3$. The density of the samples obtained are given in table 1.

| Batch | Theoretical density (TD) | Density $\rho$ (g/cm$^3$) | % of TD |
|-------|--------------------------|--------------------------|--------|
| R     | 10.96                    | 10.56                    | 96     |
| G     | 10.80                    | 9.78                     | 91     |
| AG    | 10.41                    | 9.62                     | 92     |

2. Determination of heat capacity
The heat capacity in the temperature range 35-1215 °C determined by differential scanning calorimetry method in accordance with standards DIN 51007, ASTM E 1269 in an atmosphere of high purity argon. Specimens have a diameter of 6 mm and a thickness of 1.5-1.6 mm. The heat capacity measurements were performed on the synchronous thermal analyzer Netzsch STA 409 CD. As a
reference were used disk of sapphire 6 mm in diameter and 1 mm thick. Relative error of the method is less than 5%. The results are shown in figure 1.

![Figure 1](image1.png)

**Figure 1.** The heat capacity of UO$_2$ samples of all batches.

It should be noted that because of the small amounts of additives difference of the specific heat values of samples from different batches is small and does not exceed the measurement error.

3. Determination of thermal diffusivity
Measurements were carried out on Netzsch LFA 427 by laser flash method in a high purity argon atmosphere. The samples had form of discs 10 mm in diameter, 2 mm thick.

Uranium dioxide thermal diffusivity values of R, G and AG batches shown in figure 2.

![Figure 2](image2.png)

**Figure 2.** Thermal diffusivity UO$_2$ samples of all batches.

From these results, it’s clear that thermal diffusivity of the samples decreases from 3 to 0.3 mm$^2$/s while temperature increasing. The thermal diffusivity of the samples with gadolinium additives is lower than that of pure uranium dioxide, but it is clear that a large influence exert form of burnable poison (Gd) is injected into the fuel. In samples of batch G gadolinium injected as Gd$_2$O$_3$, and during sintering it dissolves in the matrix and forms a solid solution with UO$_2$, which as known negatively affect on the thermal conductivity. In the samples of batch AG gadolinium is in the form of a perovskite phase AlGdO$_3$, and does not introduce distortion into UO$_2$ lattice, resulting in only a slight reduction in thermal conductivity compared to pure uranium dioxide in figure 2.
4. The calculation of the thermal conductivity

From the obtained data of thermal diffusivity, specific heat and density using the expression (1) were calculated temperature dependence of the thermal conductivity.

\[ \lambda(t) = a(t) \cdot C_p(t) \cdot \rho(t). \]  

Obtained data are recalculated to 95% TD by the expression

\[ \rho_p = \rho_{100} (1 - p)^{2.5}. \]

The results are shown in figure 3.

![Figure 3](image)

**Figure 3.** The temperature dependence of the thermal conductivity of samples UO₂.

The thermal conductivity of the samples is in the range 2 - 6.5 W/(m·K). Also we can see that dopants of AlGdO₃ much weaker affect on the thermal conductivity UO₂ than Gd₂O₃ one.

5. SEM-study UO₂ samples

The state of gadolinium in the samples G and AG confirmed by SEM (figures 4, 5 and tables 2, 3).

In Figure 4 - the microstructure of the sample AG in secondary electrons, UO₂ looks light gray, AlGdO₃ - dark gray. From the distribution map Gd, and gained spectra shows that all gadolinium is in AlGdO₃ form. From Figure 5, which shows the microstructure in the secondary electron and gadolinium distribution for sample batch G seen that gadolinium is evenly distributed throughout the matrix UO₂.

![Figure 4](image)

**Figure 4.** SEM image and distribution map of gadolinium in the sample batch AG.
Table 2. Composition data of the sample batch AG (wt.%)

| Spectrum  | O    | Al  | Si   | Gd  | U    |
|-----------|------|-----|------|-----|------|
| 1         | 12.42| 0.47|       |     | 87.10|
| 2         | 32.29| 31.82| 2.28 | 12.31| 21.30|
| 3         | 31.27| 35.16| 8.58 | 29.72|      |
| 4         | 12.73| 27.83| 12.92| 20.65|      |
| 5         | 12.53| 87.27|      |      |      |
| 6         | 11.76| 4.77 | 83.48|      |      |
| 7         | 16.94| 4.71 | 6.86 | 71.49|      |
| 8         | 9.49  | 1.35| 0.51 | 4.90 | 86.75|
| 9         | 5.16  | 5.16| 85.69|      |      |
| 10        | 27.30| 4.39| 68.30|      |      |

6. Conclusions
In the present work measured basic thermophysical characteristics oxide fuel with additives burnable neutron absorber in the form of a perovskite phase (Al, Gd) O$_3$ and in the form of a solid solution UO$_2$ - Gd$_2$O$_3$. State of gadolinium in the samples is confirmed by SEM-studies (figures 5, 6).

It is shown that the thermal conductivity of the samples decreases with increasing temperature and is in the range of 2-6.5 W / (m·K), moreover serious influence exert gadolinium state in UO$_2$: formation of a solid solution UO$_2$ - Gd$_2$O$_3$ causes distortion of UO$_2$ crystal lattice and as a result, a strong decrease (35%) of thermal conductivity. Gadolinium in the form of perovskite phase does not make distortion into the lattice and thermal conductivity decreased less than 5% in the entire investigated temperature range.

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