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Thermophysical Properties of Uranium-Based Niobium and Zirconium Alloys from 23 °C to 175 °C

D. M. Camarano · F. L. Migliorini ·
E. H. C. Silva · P. A. Grossi · W. B. Ferraz ·
J. B. de Paula

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Abstract The thermal diffusivities of uranium alloys were measured by the laser-flash method between room temperature and 448 K. In recent years, several UZrNb alloys have been studied by many researchers and it was shown that additions of niobium and zirconium improve the properties of uranium-based alloys. The purpose of this article is to summarize the thermophysical properties of two uranium alloys that have been studied by CDTN in a program of development of fuel for low-power reactors. The nominal compositions of the studied alloys are U4Zr6Nb and U3Zr9Nb. The results obtained by the original laser-flash method and by the mathematical model developed by the laboratory were compared to the literature data. The adaptive Monte Carlo method was used to obtain the endpoints of the probabilistically symmetric 95 % coverage interval for estimates of the output quantities and its uncertainties.

Keywords Flash method · Nuclear fuels · Thermophysical properties · Uranium–zirconium–niobium

1 Introduction

Certain alloys of uranium containing transition metals are of considerable interest in the development of nuclear fuels with low enrichment uranium for high-neutron-flux research reactors or low-power reactors. In recent years UZrNb alloys have been studied by many researchers [1–3]. It has been known that additions of niobium and zirconium improve the properties of uranium-based alloys. Uranium alloyed with Zr has excellent corrosion resistance and dimensional stability during thermal cycling;

D. M. Camarano (✉) · F. L. Migliorini · E. H. C. Silva · P. A. Grossi · W. B. Ferraz · J. B. de Paula
Comissão Nacional de Energia Nuclear/Centro de Desenvolvimento da Tecnologia Nuclear,
Av. Presidente Antônio Carlos, Belo Horizonte 6627, Brazil
e-mail: dmc@cdtn.br

uranium alloyed with niobium also improves corrosion resistance and allows tailoring of mechanical properties including strength and ductility. Uranium alloys have been studied by CDTN (Centro de Desenvolvimento da Tecnologia Nuclear) in a program of development of fuel for low-power reactors [4]. The laser-flash method [5] was adopted for the measurement of thermal diffusivity. In this method, the front face of a small wall-shaped sample receives a pulse of radiant energy coming from a laser. In practice, several factors affect the temperature transient. Numerous corrections have been introduced to account for heat losses during the process, the finite laser pulse, the non-uniform heating of the sample, and other factors interfering on the experiment [6]. Among them, thermal loss is the most significant [7–9]. A mathematical model [10] based on this method was developed to obtain the thermophysical property values considering the solution of the one-dimensional heat transfer equation. In this study, an effective methodology for uncertainty evaluation of thermophysical properties based on the flash method was used. The methodology is based on the Monte Carlo method (MCM) [11] applied to a central thermal-diffusion model that considers all real initial and boundary conditions from a physical model (experimental bench based on flash method). Consequently, additional corrections are not needed. The GUM uncertainty framework (Guide to the Expression of Uncertainty) [12] was used to obtain the associated standard uncertainty with an estimate of the input quantities. The data on thermal diffusivity, thermal conductivity, and specific heat of Zr and Nb based-uranium alloys from room temperature to 448 K are presented and discussed.

2 Measurements

2.1 Sample

The alloys of uranium were obtained by vacuum induction melting using a graphite crucible and cast into a cylindrical copper ingot mold. Samples from 25 mm in diameter and 3 mm in thickness were cut from the as-cast alloy. These samples were homogenized in a vacuum of $<10^{-4}$ Torr at a temperature of 1 273 K during 24 h under a controlled heating rate of $3\ \text{K}\cdot\text{min}^{-1}$ and were cooled under vacuum until they reached room temperature. The starting materials were uranium of technical purity with about 500 ppm of metallic impurities, zirconium of 99.8 % purity, and niobium of 99.9 % purity. These alloys were then reheated to the gamma phase at about 1 073 K, for 1 h. After the samples were quenched in a tin bath at 573 K, they were subjected to aging treatments ranging from about 4 min to 48 h [4].

2.2 Procedures

Figure 1 shows a schematic drawing of an experimental apparatus for thermal-diffusivity measurements using the flash method. As shown in the figure, the apparatus is composed of a sample holding device, a heating furnace, a CO_2 laser (of 100 W total power) working at 10.6 μm wave length, an infrared thermometer, a vacuum pump, and measuring control and data processing systems. An infrared thermometer measures the transient temperature, and the thermal radiance signal is digitized using a 16 bit

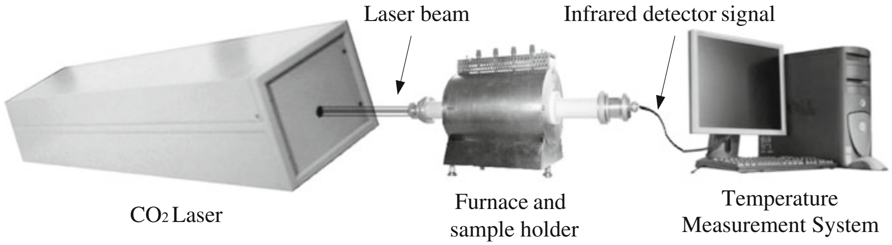

Fig. 1 Thermophysical properties measurement laboratory experimental apparatus

A/D converter of an NI PCI-6052 data acquisition device. LabView programming is used to acquire data. The sample (8 mm in diameter and about 2.5 mm in thickness) is placed in a vacuum furnace and isothermally heated. In order to avoid any transmission of the laser beam through the samples, a thin carbon layer was applied over the front surfaces. The rear surfaces of the samples were also coated to ensure a uniform emissivity. The system allows irradiation of the front face of the sample obtaining a register of the rear face transient temperature of the sample. The apparatus is specially designed to operate under conditions imposed to measure the thermal diffusivity of nuclear fuels.

Thermal-diffusivity measurements were carried out employing the laser-flash technique [5] from room temperature to 448 K. The data were limited to this range of temperature because this is within the range of interest, which is up to 573 K. An important feature in the determination of the thermal diffusivity of radioactive nuclear fuel is the need to keep the temperature increase in the sample as low as possible, in particular, the sharp temperature increase in the front surface of the samples. Measurements were carried out with constant laser pulse energies, which produced rear-surface temperature excursions from 1.9 K to 2 K. In order to check the accuracy of the thermal-diffusivity measurement system, we used a graphite sample [13] as reference. Besides that, an Inconel 600 standard [14] was used as a reference only to verify the performance of the experimental apparatus considering that its properties are closely similar to those of the UZrNb alloys. The maximum deviation of all mean values determined by the LMPT (Laboratório de Medição de Propriedades Termofísicas) from the certified value is in the range of 4 % for the graphite and of 2 % for the Inconel 600 standard, which is within the mutual uncertainty of the values.

2.3 Uncertainty of Measurement

The sources of uncertainties in the measurement are associated with the sample itself, the temperature measurement, time measurement, the non-uniform heating of the sample, and heat losses [15,16].

2.3.1 Uncertainties Associated with the Sample

The uncertainty of sample thickness is the result of the following sources of uncertainties: repeatability of measurements, correction of thermal expansion, resolution, calibration, and drift of micrometer. This uncertainty was calculated based on the thermal expansion coefficient of $9.78 \times 10^{-6}\,\mathrm{K}^{-1}$ of solid UO_2 [17] and a temperature gradient equal to 3 K. The uncertainty of the linear expansion coefficient from room temperature to 448 K was assumed to be $0.05 \times 10^{-6}\,\mathrm{K}^{-1}$. The uncertainty in thermal diffusivity resulting from the thickness measurement was estimated to be less than 0.1 %.

2.3.2 Uncertainties Associated with the Temperature

The temperature of the sample is not considered in the thermal-diffusivity estimation, but the uncertainty of the half-time, and consequently, the uncertainty of the thermal diffusivity depend on the temperature sample. The uncertainty of a radiation thermometer results from the uncertainty due to resolution, calibration, drift, time constant, and other factors such as the effective emissivity of the sample, stability, and the homogeneity of the furnace temperature. The samples were coated on both sides with carbon film to improve and control the emissivity and absorptivity of the sample. The uncertainty in temperature due to the sample emissivity was estimated to be less than 2 % [18]. The uncertainty in the sample temperature was estimated to be 0.2 %.

2.3.3 Uncertainties Associated with the Time Scale/Finite Pulse-Time Effect

The uncertainty on the time measurement results from the combination of the uncertainties due to measurement instruments and the data acquisition board. A computer simulation program was used to estimate the influence of the finite pulse-time effect on the thermal diffusivity. The uncertainty in the thermal diffusivity resulting from the time scale and finite pulse-time effect was estimated to be 1.5 %.

2.3.4 Uncertainties Associated with Non-Uniform Heating

The uniformity of a laser pulse may change from shot-to-shot, and it is also dependent on the energy level of the laser beam. A 3 % uncertainty due to the effect of non-uniform heating was assumed in the uncertainty budget [19].

2.3.5 Uncertainties Associated with the Heat Losses

The contribution of the heat losses is expressed by an overall heat transfer coefficient. Computational simulations were used to estimate the influence of the heat losses on the thermal diffusivity. In all cases, the influence of heat losses on the thermal-diffusivity accuracy was estimated to be 2 % [10].

2.4 Mathematical Modeling

The numerical solution for the heat diffusion on the laser-flash experiment is based on a mathematical domain considering the real initial and boundary conditions of LMPT experimental apparatus, in which a thin disk sample is intensely heated on its frontal face by a short laser pulse. This complex heat diffusion process encompassing laser pulse-time effects, non-adiabatic conditions, and dynamic effects of the temperature measurement system was analyzed and modeled by the LMPT staff. From measurements of thermal transients on the rear face of the sample, the thermophysical properties were evaluated based on the principles of the laser-flash method.

The finite volume method [20] was applied to solve inverse heat conduction problems [21,22] and obtain numerical solutions of the thermal diffusion process considering real experimental conditions [10]. In order to obtain the numerical solutions of the heat diffusion on the laser-flash experiment, stochastic modeling based on the MCM [11] was used to accomplish an uncertainty evaluation for all parameters considered by the model [10]. A value of $M = 15$ (number of Monte Carlo trials) was used by the adaptive procedure in this study.

3 Results

All thermal-diffusivity values presented here result from the average of five successive measurements carried out on repeatability conditions. Tables 1–3 show, respectively, the thermal diffusivity, thermal conductivity, and specific heat of UZrNb alloys as a function of temperature. The thermal-diffusivity values in this experiment increased with increasing temperature, in both alloys. The thermal conductivity of UZrNb alloys, shown in Table 2, increases smoothly with increasing temperature. The results showed a similar trend as experimental data reported by Kollie et al. [23] for which two alloys of uranium-based Mo, Nb, Zr, and Ti were used for comparison. In this study, the thermal-conductivity values increased with increasing temperature. In Table 3, the specific heat of UZrNb alloys was found to be a function of temperature. We noticed that the observed values of the heat capacity decreased with increasing temperature. The results showed that the thermal diffusivity and thermal conductivity of the U6Zr4Nb alloy were lower than U3Zr9Nb. By comparison, probabilistically and symmetrically, a 95 % coverage interval for the thermal diffusivity, thermal conductivity, and specific heat of the U3Zr9Nb alloy obtained by the MCM was higher than that obtained with U4ZrNb. The probable cause of this effect was due to the scatter in the data of alloy U3Zr9Nb. In this case we need further experiments. The application of the MCM for $M = 15$ trials was suitable in practice having an affordable computational time. Although the use of a small value of M is inevitably less reliable than that of a large value, we assigned a Gaussian probability density function to characterize the knowledge for output quantities. Therefore, this uncertainty can be considered for a worst-case test situation.

4 Conclusions

Selected thermophysical properties (thermal diffusivity, thermal conductivity, and specific heat) of two kinds of UZrNb alloys were determined using a mathematical model based on the laser-flash method. The experimental results show that the two alloys have small differences in thermophysical properties. The thermal diffusivity and thermal conductivity of alloy UZrNb increase with increasing temperature.

Table 1 Thermal diffusivity of UZrNb alloys

Temperature (K)	Thermal diffusivity ($mm^2 \cdot s^{-1}$)			
	U4Zr6Nb		U3Zr9Nb	
	Mean value	95 % Coverage interval	Mean value	95 % Coverage interval
298	3.81	0.13	4.69	0.45
323	4.20	0.20	5.26	0.73
348	4.45	0.30	5.78	0.68
448	5.45	0.29	7.14	0.73

Table 2 Thermal conductivity of UZrNb alloys

Temperature (K)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)			
	U4Zr6Nb		U3Zr9Nb	
	Mean value	95 % Coverage interval	Mean value	95 % Coverage interval
298	15.0	1.1	17.5	1.1
323	16.5	0.9	18.0	1.3
348	17.0	0.8	18.4	0.9
448	20.4	0.5	21.5	1.2

Table 3 Specific heat of UZrNb alloys

Temperature (K)	Specific heat ($J \cdot kg^{-1} \cdot K^{-1}$)			
	U4Zr6Nb		U3Zr9Nb	
	Mean value	95 % Coverage interval	Mean value	95 % Coverage interval
298	274	21	244	18
323	272	23	224	22
348	264	18	208	20
448	259	13	198	15

Comparison of the results with literature data gives insight into the accuracy of the techniques employed. The developed mathematical model shows it to be an efficient tool to implement the corrections for all experimental problems associated with the flash method, encompassing evaluation of the thermal conductivity, specific heat, and its assigned uncertainties based on the MCM. It should be noted, however, that other uncertainties still remain to be evaluated, such as the effect of the coefficient of thermal expansion of the alloys. The thermal expansion of nuclear fuel is one of the most important properties because it affects the gap conductance. It also causes a density variation with temperature, which is used for the calculation of other properties, such as thermal conductivity. Uranium with zirconium and niobium produces a series of alloys, whose properties can be markedly changed by heat treatment. So, the obtained data can be seen as preliminary work on the thermophysical properties of uranium-based Zr and Nb alloys. A more detailed investigation becomes necessary to study the correlation of the effect of different kinds of heat treatment on the thermophysical properties, and also to compare the GUM uncertainty framework and MCM.

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References

1. C.B. Basak, R. Keswani, G.J. Prasad, H.S. Kamath, N. Prabhu, J. Alloys Compd. **471**, 544 (2009)
2. H.L. Yakel, J. Nucl. Mater. **33**, 286 (1969)
3. R.H. Cooper, Jr., A study of retention of metastable phases in quenched uranium-niobium-zirconium ternary alloys. Report Number: Y-1984 (Oak Ridge National Laboratory, 1975)
4. L.P.A.R Tanure, N.M Cantagalli, M.B. Ferraz, A.M.M Santos, in *Proceedings of the International Nuclear Atlantic Conference*, Rio de Janeiro, Brazil (ABEN, Rio de Janeiro, 2009)
5. W.J. Parker, R.J. Jenkins, C.P. Bulter, G.L. Abbott, J. Appl. Phys. **32**, 1679 (1961)
6. ASTM Test Method E 1461-07, *Standard Test Method for Thermal Diffusivity of Solids by the Flash Method* (American Society for Testing and Materials, West Conshohocken, PA, 2007)
7. L.M. Clark, R.E. Taylor, J. Appl. Phys. **46**, 714 (1975)
8. T. Baba, A. Ono, Meas. Sci. Technol. **12**, 2046 (2001)
9. G.A. Longo, Int. J. Thermophys. **29**, 664 (2008)
10. P.A. Grossi, Ph.D. thesis, Federal University of MinasGerais, Brazil, 2008
11. Joint Committee of Guides in Metrology (JCGM), Evaluation of Measurement Data—Supplement 1 to the Guide to the Expression of Uncertainty in Measurement—Propagation of Distributions using a Monte Carlo Method, JCGM 101:2008 (JCGM, 2008)
12. Joint Committee of Guides in Metrology (JCGM), Evaluation of Measurement Data—Guide to the Expression of Uncertainty in Measurement, JCGM 100:2008 (JCGM, 2008)
13. LNE, in Test Report, Graphite Sample, Laboratorie National de Métrologie et D′Essais (2009)
14. J. Blumm, A. Lindemann, in Manufacture's Certification, Thermophysical Properties Standard—Inconel 600, NETZSCH Gerätebau GmbH Applications Laboratory (2009)
15. F.L. Migliorini, E.H.C. Silva, P.A. Grossi, R.A.N. Ferreira, D.M. Camarano, in *Proceedings of the XIX IMEKO World Congress*, Lisbon, Portugal (IMEKO, Lisbon, 2009)
16. B.P. Hay, J.R. Filtz, J. Hameury, L. Rongione, Int. J. Thermophys. **26**, 6 (2005)
17. J.K. Fink, J. Nucl. Mater. **279**, 1 (2000)
18. K. Chrzanowski, in *Non-Contact Thermometry—Measurement Errors* (SPIE Polish Chapter, Poland, 2001)
19. A. Cezairliyan, T. Baba, R.E. Taylor, Int. J. Thermophys. **15**, 317 (1994)
20. S.V. Patankar, in *Numerical Heat Transfer and Fluid Flow* (Hemisphere, New York, 1980), p. 353
21. D.G. Luenberger, in *Linear and Nonlinear Programming*, 2nd edn. (Addison-Wesley, New York, 1984), p. 491
22. M.N. Özişik, in *Heat Conduction*, 2nd edn. (Wiley-Interscience, Raleigh, 1993), pp. 571–616
23. T.G. Kollie, J.P. Moore, D.L. McElroy, H.L Whaley, R.K. Williams, T.G. Godfrey, W.M. Ewing, R.S. Graves, Report Number: ORNL-TM-4253, Oak Ridge National Laboratory (1973)