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Corrosion of steel claddings of fast reactors fuel elements in the interaction with uranium-plutonium nitride fuel

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Introduction

Nuclear fuel and structural materials used in nuclear reactors are complex objects as far as thermodynamic modeling is concerned.

An issue about the possibility to describe nuclear fuel properties using the mathematical apparatus of equilibrium thermodynamics deserves special consideration. Generally speaking, the thermodynamic equilibrium state suggests that there are no any flows (of mass, energy or momentum) in the system under study. It is quite possible to achieve such a state of the system in mixed nitride fuel fabrication processes. In operating conditions, however, heat transfer processes take place in fuel elements due to existing temperature gradients. Besides, strong temperature dependence of some chemical reaction constants will result in non-uniform distribution of fuel components and fission products over fuel pellets, giving rise to diffusion flows of substance. All this imposes significant constrains on applicability of thermodynamics to the object under study, and calls for a thorough analysis of the range of applicability of thermodynamics in operating conditions.

Generation of atoms via nuclear reactions

Nuclear generation of components, serves as a source, and is not a relaxation process. However, when studying a change in chemical composition in the neighborhood of some fuel point due to nuclear generation, a question arises about the time it takes to reach a local equilibrium, i.e. the time during which a certain concentration will be attained, which will allow introducing statistical thermodynamic values.

A local equilibrium in the neighborhood of some point depends on the characteristic size of the domain containing ~ 10^2 - 10^3 particles of the kind under consideration. This value corresponds to replacement of statistical factorial expressions of thermodynamic functions by their Stirling's logarithmic approximation with an accuracy of about a few percent. In particular, in our case the rate of generation of main elements is ~ 10^{18} - 10^{19} at/s·m^3.

Let us estimate characteristic time of the establishment of local equilibrium τ^* in the extreme points of the temperature range under consideration (873 – 1773K).

The characteristic time of the establishment of local equilibrium

Diffusion parameters for diffusion coefficients of Cs, Ag and Sr and characteristic times required to attain local equilibrium, which were calculated from the diffusion parameters for two temperature levels are presented in Table 1.

Table 1. Diffusion parameters and characteristic times for Cs, Ag and Sr

Chemical element	D_o m^2/s	Q kJ/ mole	D_{873K} m^2/s	D_{1773K} m^2/s	τ^* (873K) s	τ^* (1773K) s
Cs	$5{,}6 \cdot 10^{-8}$	209	$1{,}7 \cdot 10^{-20}$	$3{,}9 \cdot 10^{-14}$	$2{,}9 \cdot 10^{5}$	44
Ag	$6{,}7 \cdot 10^{-9}$	165	$8{,}7 \cdot 10^{-19}$	$9{,}2 \cdot 10^{-14}$	$2{,}7 \cdot 10^{4}$	26
Sr	$2{,}2 \cdot 10^{-3}$	488	$1{,}2 \cdot 10^{-32}$	$9{,}2 \cdot 10^{-18}$	$5{,}7 \cdot 10^{15}$	$0{,}7 \cdot 10^{4}$

According to the above estimates, almost in all cases considered, except for strontium at the lower temperature, the local equilibrium is attained in a quite acceptable time. However, in case of strontium at 873K, this time approaches $1.8 \cdot 10^{8}$ years. Hence thermodynamic calculations of elements with very low coefficients of diffusion shall be treated with caution.

Some peculiarities of the uranium-plutonium nitride fuel thermodynamics during the burnup process

Thermodynamic analysis of some anomalies in behavior of the phase and chemical composition of the mixed nitride fuel at different levels of burnup was performed using the IVTANTHERMO computer code [1].

Chemical thermodynamics studies of the multicomponent systems being considered are based on the use of the elemental composition of the nuclear fuel in the course of its irradiation, which was obtained from neutronics calculations. This paper deals with the (U-Pu)N fuel composition containing 13.4 wt. % of plutonium.

For calculation of the thermodynamic equilibrium, there was considered a system where all condensed components were divided into 2 solutions, while individual phases were used for the other components. The condensed phase of the fresh fuel consists of the following elements and compounds: U, UN, $UN_{1.466}$, $UN_{1.54}$, $UN_{1.73}$, Pu and PuN. Oxygen and carbon may be found in the fuel as impurities due to the fabrication process. The given system at burnup contains a very large number of various compounds (over 250). Therefore, due to limitations of the computer code used, some of the compounds were removed in the course of the calculations.

1. Belov G.V. Calculation of equilibrium composition and properties of thermodynamic systems under elevated pressure. Mathematical modeling, 2001. V13, No.8.

Neutronic calculation of the isotopic composition

At the initial stage the calculation of the isotopic composition of fuel at various values of burnup was conducted (code ISTAR-2.06).

Table 2. Molar compositions for basic elements (BN-1200)

Chemical element	Mole					
	0% FIMA,	4% FIMA	8% FIMA	9,3% FIMA	12% FIMA	16% FIMA
U	2,6738E+00	2,5473E+00	2,4209E+00	2,3797E+00	2,2944E+00	2,1679E+00
Pu	4,1244E-01	4,2989E-01	4,3760E-01	4,3844E-01	4,3812E-01	4,3396E-01
Xe	0	3,1211E-02	6,2440E-02	7,2590E-02	9,3677E-02	1,2408E-01
I	0	2,4114E-03	4,5596E-03	5,2578E-03	6,6349E-03	8,5512E-03
Te	0	4,4037E-03	8,8531E-03	1,0299E-02	1,3317E-02	1,7677E-02
Cs	0	2,7451E-02	5,3654E-02	6,2170E-02	7,9281E-02	1,0341E-01
Sr	0	1,2689E-02	2,6201E-02	3,0592E-02	4,0248E-02	5,4672E-02
Zr	0	2,4353E-02	4,7994E-02	5,5678E-02	7,1648E-02	9,4678E-02
Ce	0	1,5030E-02	2,7779E-02	3,1922E-02	4,0456E-02	5,2718E-02
Y	0	2,4434E-03	4,6972E-03	5,4296E-03	6,9399E-03	9,1071E-03
La	0	3,9191E-02	8,0813E-02	9,4290E-02	1,2248E-01	1,6312E-01
Ru	0	4,2629E-02	8,1798E-02	9,4528E-02	1,2043E-01	1,5731E-01
Ag	0	1,2590E-03	2,5005E-03	2,9040E-03	3,7445E-03	4,9603E-03
Cd	0	2,2198E-03	4,5661E-03	5,3286E-03	6,9828E-03	9,4394E-03
Mo	0	2,6389E-02	5,3468E-02	6,2268E-02	8,0421E-02	1,0647E-01
C	0	7,7773E-03	1,5590E-02	1,8129E-02	2,3402E-02	3,1215E-02
N	3,0798E+00	3,0673E+00	3,0549E+00	3,0509E+00	3,0425E+00	3,0301E+00

The impurities of oxygen and carbon

Oxygen and carbon were introduced additionally as impurities.

Table 3. Number of moles of oxygen impurities

wt.%	Oxygen impurities, mole					
	0% FIMA	4% FIMA	8% FIMA	9,3% FIMA	12% FIMA	16% FIMA
0,05	0,0243	0,0244	0,0244	0,0244	0,0244	0,0243
0,1	0,0486	0,0488	0,0488	0,0488	0,0488	0,0486
0,15	0,0729	0,0732	0,0733	0,0732	0,0731	0,0729
0,2	0,0973	0,0976	0,0977	0,0976	0,0975	0,0971
0,25	0,1216	0,1220	0,1221	0,1221	0,1219	0,1214
0,3	0,1459	0,1464	0,1465	0,1465	0,1463	0,1457

Table 4. Number of moles of carbon impurities

wt.%	Carbon impurities, mole					
	0% FIMA	4% FIMA	8% FIMA	9,3% FIMA	12% FIMA	16% FIMA
0,05	0,0324	0,0325	0,0326	0,0325	0,0325	0,0324
0,1	0,0648	0,0651	0,0651	0,0651	0,0650	0,0648
0,15	0,0973	0,0976	0,0977	0,0976	0,0975	0,0971
0,2	0,1297	0,1301	0,1302	0,1302	0,1300	0,1295
0,25	0,1621	0,1627	0,1628	0,1627	0,1625	0,1619
0,3	0,1945	0,1952	0,1953	0,1953	0,1950	0,1943

Let us now consider some features of the thermodynamics of (U, Pu)N fuel.

Temperature dependences of the uncombined uranium content in the fresh fuel

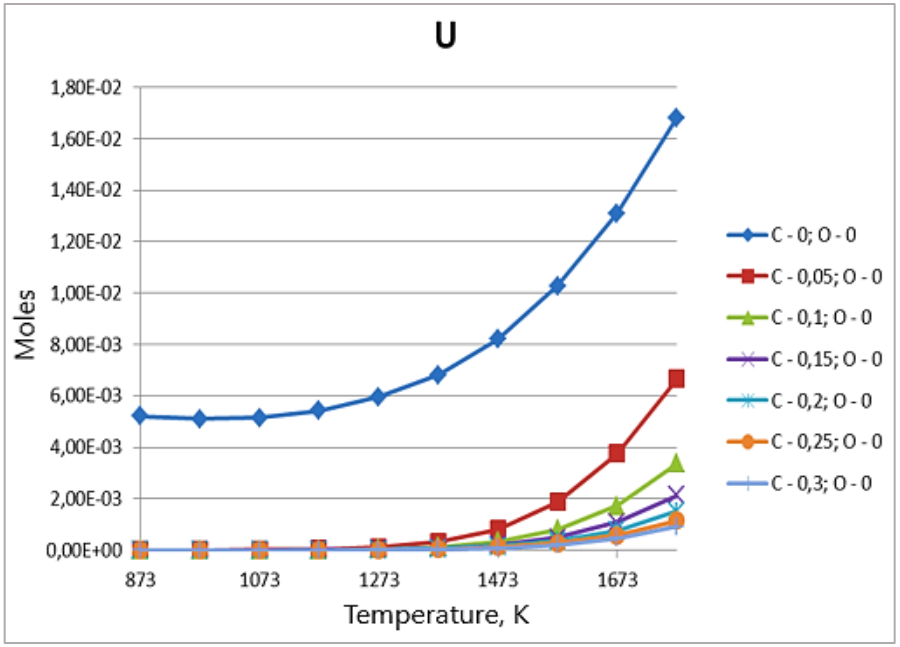

Fig. 1 – Unbound U content in the fresh fuel in the absence of oxygen at various concentrations of carbon impurity (0 - 0.3 wt.%) versus of temperature

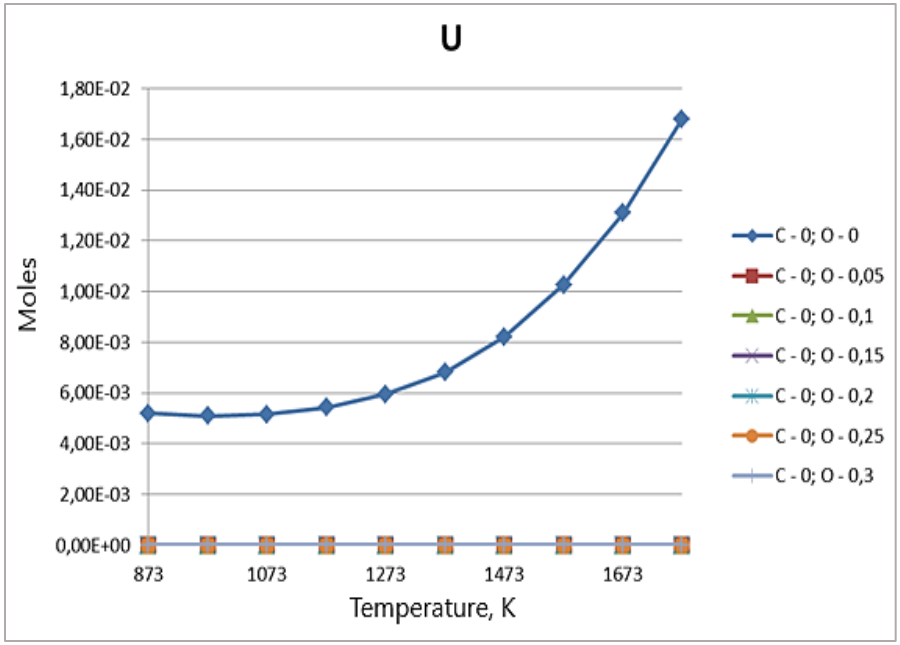

Fig. 2 – Unbound U content in the fresh fuel in the absence of carbon at various concentrations of oxygen impurity (0 - 0.3 wt.%) versus of temperature

According to Figures 1 and 2, the presence of the C and O impurities dramatically reduce the uncombined uranium content in the fresh fuel. This may result in a substantial suppression of uranium transfer processes in the fuel.

Temperature dependences of the uncombined plutonium content in the fresh fuel

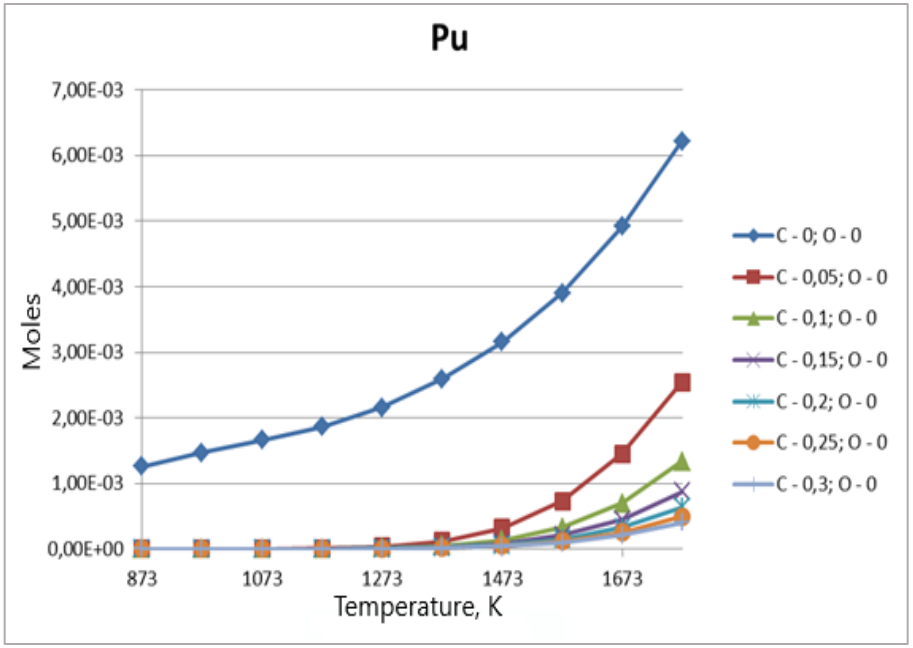

Fig. 3 – Unbound Pu content in the fresh fuel in the absence of oxygen at various concentrations of carbon impurity (0 - 0.3 wt.%) versus of temperature

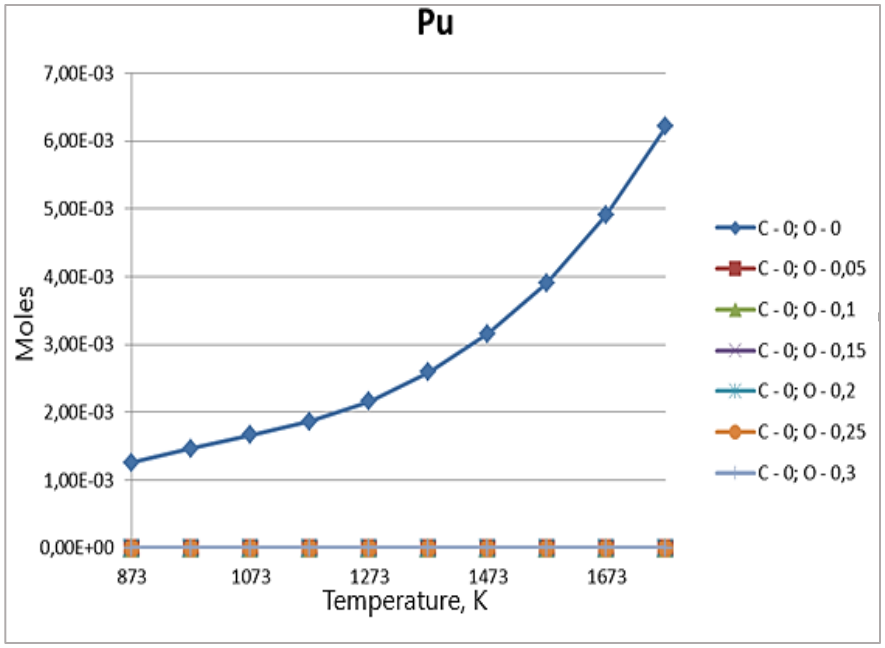

Fig. 4 – Unbound Pu content in the fresh fuel in the absence of carbon at various concentrations of oxygen impurity (0 - 0.3 wt.%) versus of temperature

The presence of the C and O impurities dramatically reduce the uncombined plutonium content in the fresh fuel too. This may result in a substantial suppression of plutonium transfer processes in the fuel.

Temperature dependences of the amount of UN and UO_2 in the fuel with 9.3% FIMA burnup

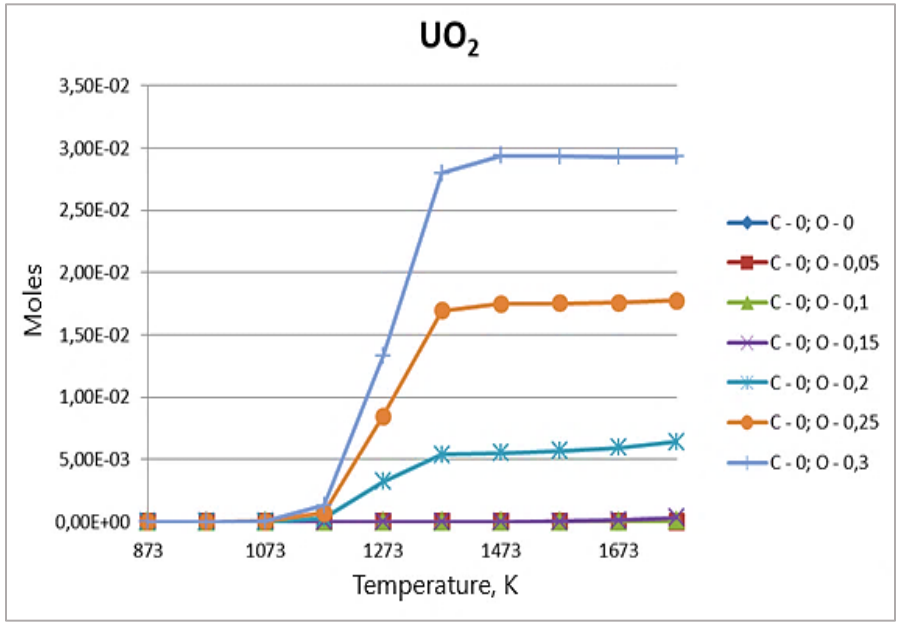

Fig. 5 – UO_2 in the fuel with burnup 9.3% FIMA in the absence of carbon at various concentrations of oxygen impurity (0 - 0.3 wt.%)

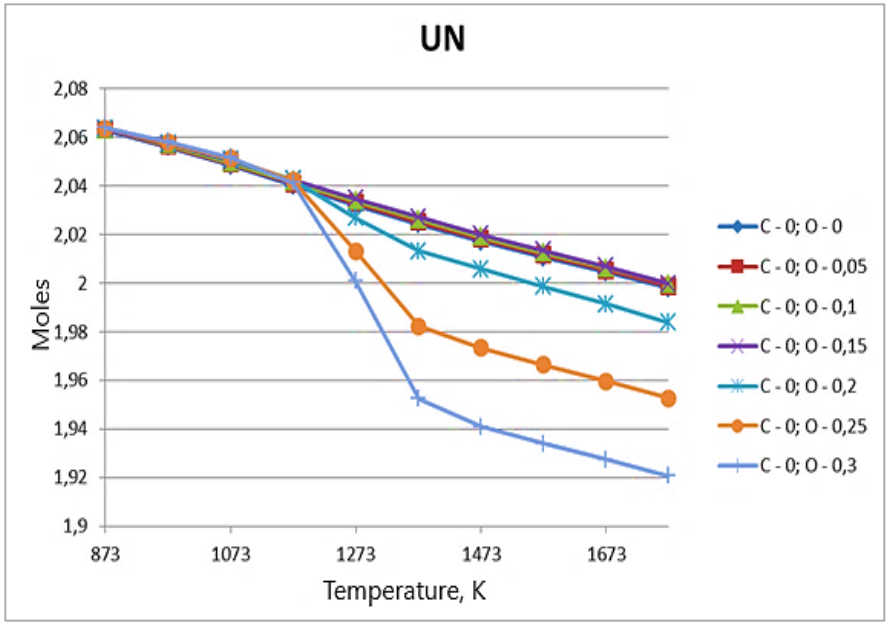

Fig. 6 – UN in the fuel with burnup 9.3% FIMA in the absence of carbon at various concentrations of oxygen impurity (0 - 0.3 wt.%)

The correlation of temperature dependences of the content of uranium oxide and nitride in the fuel is obvious.

The effect of the ultimate solubility of carbon

UN content as a function of carbon concentration for various oxygen concentrations (0 - 0.3 wt.%) are presented in Figures 7 and 8.

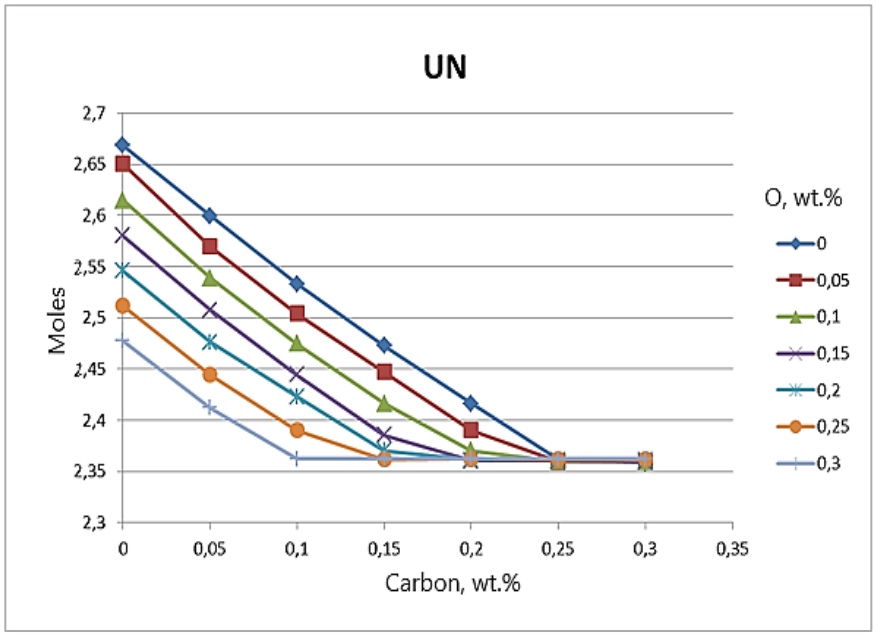

Fig. 7 – UN in the **fresh** fuel depending on the carbon concentration at a temperature of 873K

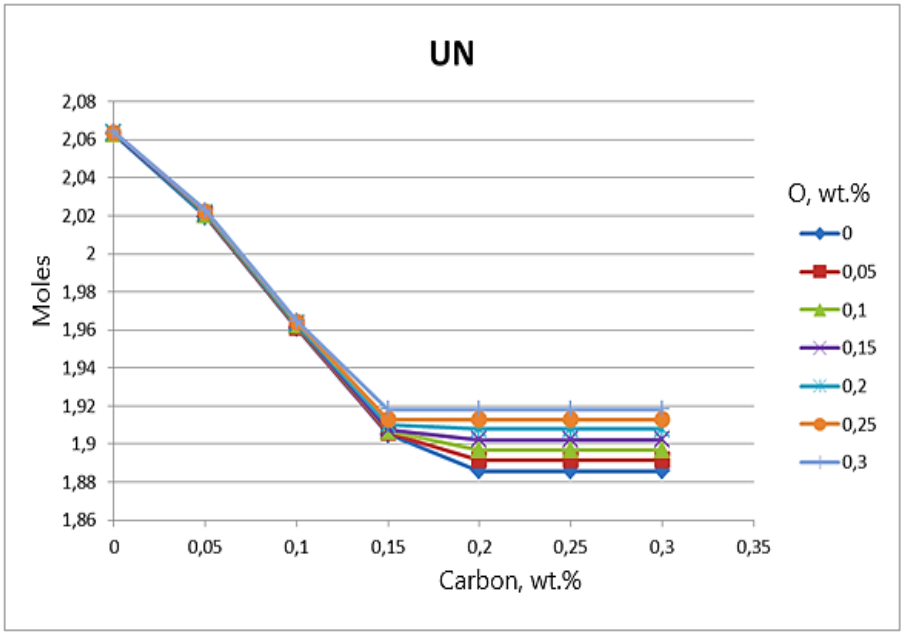

Fig. 8 – UN in the fuel irradiated to the burnup of **9.3%** FIMA depending on the carbon concentration at a temperature of 873K

According to these Figures with increasing carbon concentration decrease in the number UN phase up to a certain limit is observed. Upon reaching this limit, a further increase in the concentration of carbon impurities does not affect the amount of UN in the fuel. In this case, the formation of uranium carbide stops, and the added carbon may remain in the unbound state.

The state of carbon in the condensed phase of the fuel at various burnup values

First of all, we consider the behavior of unbound carbon in the solid phase of fuel. Unbound carbon can easily move into the steel cladding of a fuel rod and lead to a degradation of the mechanical characteristics of steel.

We have shown that the carbon present in the composition of the fuel can be under certain conditions, both in the bound state in the form of carbides, carbonates or other compounds of the components of the fuel with carbon, and dissolved in the fuel in the unbound form.

Relative fraction of unbound carbon in the initial fuel at temperatures of 873 and 973K and various mass fractions of carbon impurities

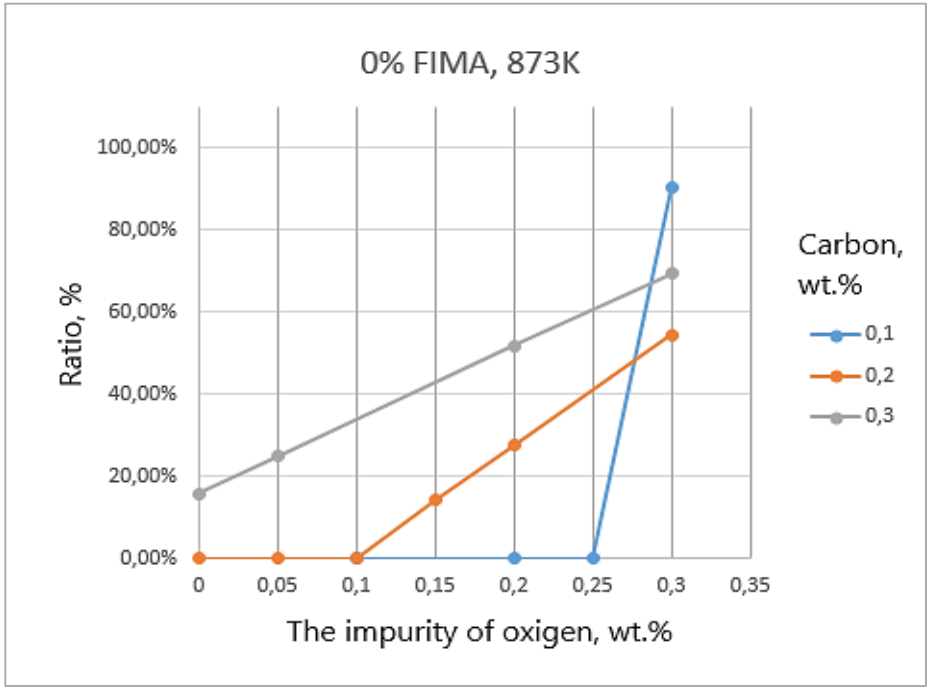

Fig. 9 – The fraction of unbound carbon in relation to the total content of carbon impurities in the initial fuel, depending on the mass fraction of oxygen impurities at a temperature of 873K

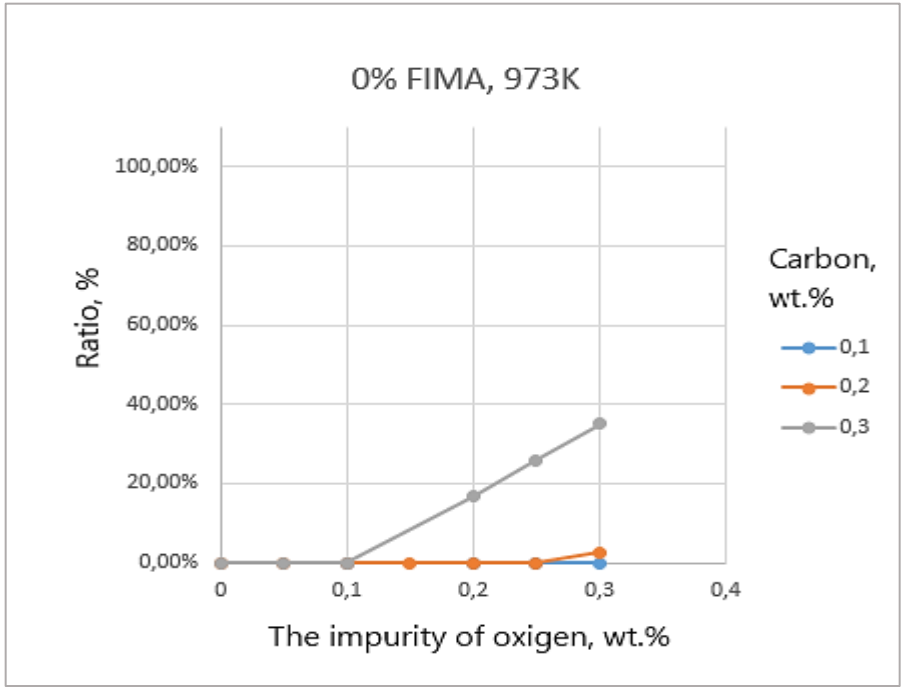

Fig. 10 – The fraction of unbound carbon in relation to the total content of carbon impurities in the initial fuel, depending on the mass fraction of oxygen impurities at a temperature of 973K

At a temperature of 873K, the fraction of unbound carbon can reach 50% or more. However, at 973K it is greatly reduced.

Relative fraction of unbound carbon for various fuel burnups

Figure 11 shows the dependences of the fraction of unbound carbon with respect to the total carbon impurity content in the fuel with different burnup.

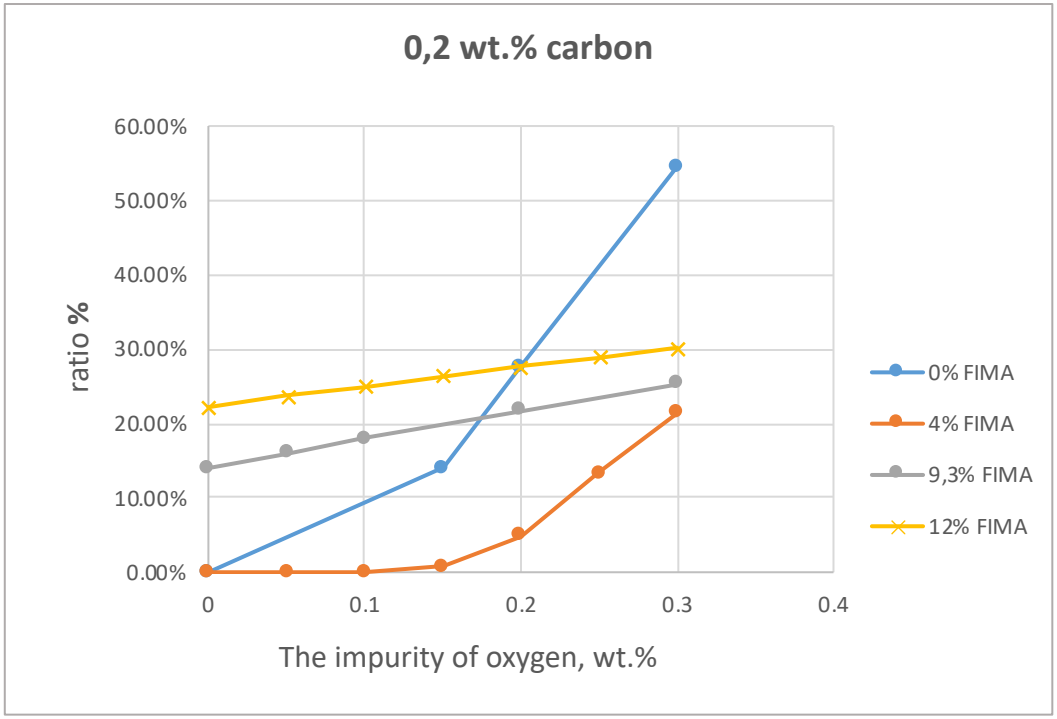

Fig. 11 – The fraction of unbound carbon with respect to the total carbon impurity content in fuel with different burnup, depending on the mass fraction of oxygen impurity at 0.2 wt.% of carbon impurity and at temperature 873K.

Thereby, the fuel is a carbon source, which can directly affect the condition of the steel cladding of the fuel element and its mechanical characteristics.

The model system “(U, Pu) N fuel + cladding from austenitic steel ChS68-ID”

On the next step of this work, we studied the thermodynamics of the model system “(U, Pu)N fuel + cladding from austenitic steel ChS68-ID” by the IVTANTERMO code.

Table 5 - The composition of the steel ChS68-ID cladding.

Chemical element	Mass fraction, wt.%	Amount, mole
Si	0,45	1,99E-02
Mn	1,65	3,72E-02
Ni	14,75	3,12E-01
S	0,01	3,87E-04
P	0,02	8,01E-04
Cr	16,25	3,88E-01
Mo	2,2	2,84E-02
V	0,2	4,87E-03
Ti	0,35	9,06E-03
Fe	64,04	1,42E+00
C	0,08	8,26E-03

Table 6 - The geometric dimensions of the cladding.

The diameter of the fuel rod, mm	9,7
Cladding thickness, mm	0,5
The gas gap between the fuel and the cladding, mm	0,15
Diameter of fuel pellet, mm	8,4
Cladding length, mm	1100

In the calculation model, it is assumed that the cladding length is equal to the fuel column height.

The calculation results of the model system: "Steel ChS68-ID + (U, Pu)N fuel with impurities C and O"

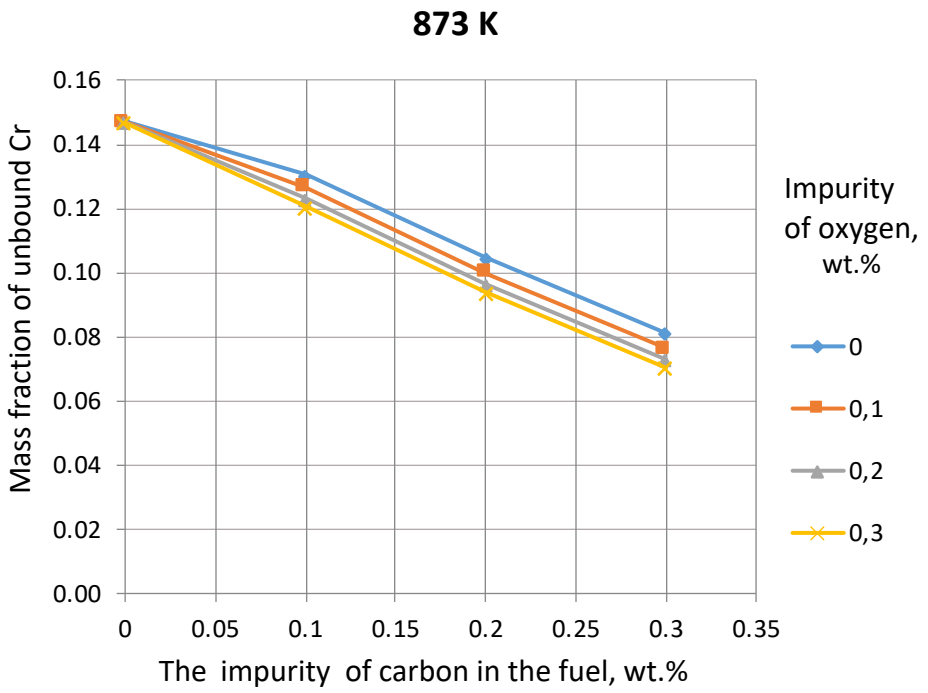

Fig. 12 – Mass fraction of unbound Cr (wt.%) in the cladding at a temperature of 873K, depending on the content of carbon impurities at different values of the concentration of oxygen impurities; 0% FIMA.

It is shown, that an increase of the carbon content in the initial fuel leads to a monotonic decrease in the average concentration of unbound chromium in the fuel cladding.

All unbound carbon in the fuel goes into the shell and is associated mainly with chromium.

The limit of passivity with respect to intergranular corrosion of austenitic steel (12 wt.% Cr) is reached at a temperature of 873K for all values of oxygen concentration and the mass fraction of carbon in the fuel is less than 0.15 wt.%.

Carbon Binding in (U, Pu)N Fuel

- The effect of unbound carbon on the steel cladding of a fuel element is most pronounced in the low-temperature part of the temperature range under consideration at maximum burn-ups and maximum concentrations of carbon and oxygen impurities, i.e. in the same areas of parameters at which the fraction of unbound carbon reaches its maximum values in the fuel.
- One of the possible ways to reduce the effect of carbon on the strength characteristics of steel claddings of fuel rods is to block its penetration into the shell.
- Binding of free carbon in the fuel by introducing into its composition a certain amount of effective carbide formers makes it possible to suppress intergranular corrosion of steel fuel cladding.

Mo and Ti as carbide-formers in (U, Pu)N fuel. Effect on the content of unbound Cr in the cladding

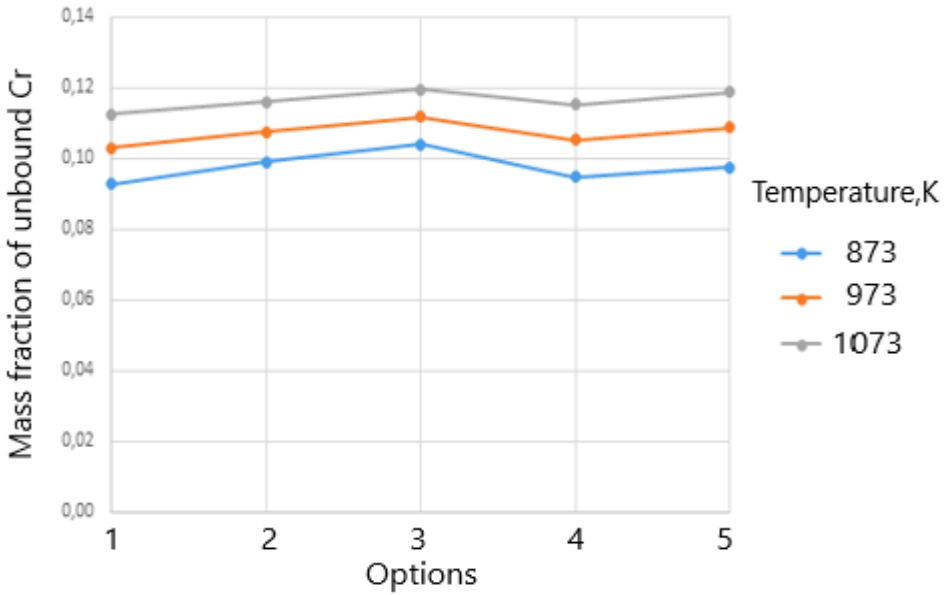

Fig. 13 – Mass fractions of unbound Cr in the ChS68-ID steel cladding in a fuel element with various options for the addition of Mo and Ti carbide-formers; 9.3% FIMA burnup.

Five options are considered:

1 - calculation without additional additives of Mo or Ti in the fuel;

2 - added 0.036 moles of Mo (≈ 0.45 wt.% Mo);

3 - added 0.072 moles of Mo;

4 - added 0.036 mol of Ti;

5 - added 0.072 moles of Ti (≈ 0.45 wt.% Ti).
0.12 is the level of passivity.

The calculation results show a rather low efficiency of both molybdenum and titanium as carbide-forming additives in the system under consideration, especially in burned (U, Pu)N fuel.
However, the use of Cr as carbide-former provides an encouraging result.

Carbide-former Cr

Mass fraction of unbound chromium (wt.%) versus on the amount of carbon impurity for 3 variants of chromium addition (0; 0.5 and 1 wt.%) at a temperature of 873 K.

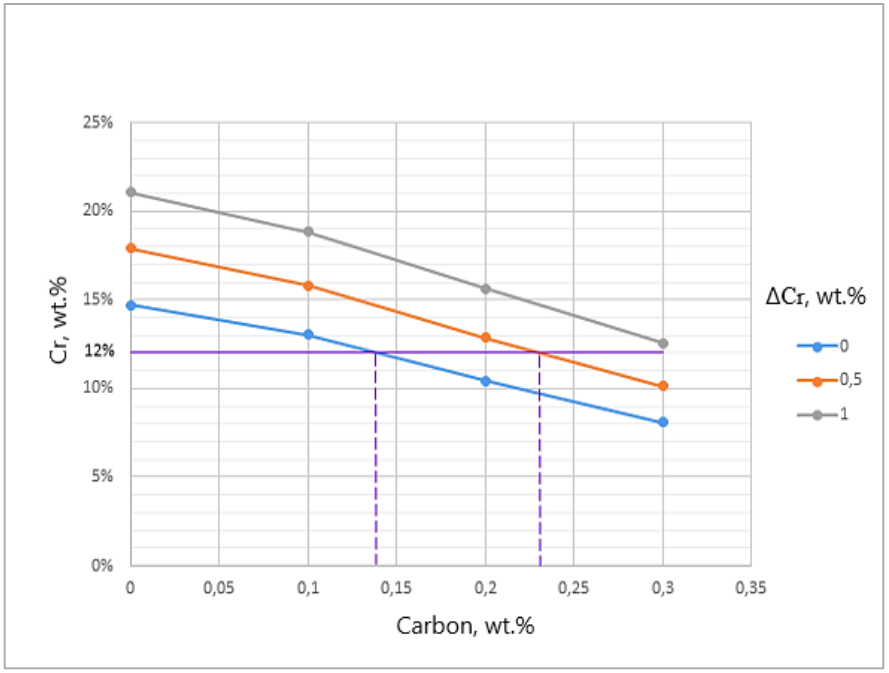

Fig. 14 - Mass fraction of unbound chromium (wt.%) versus on the amount of carbon impurity; **0%** FIMA

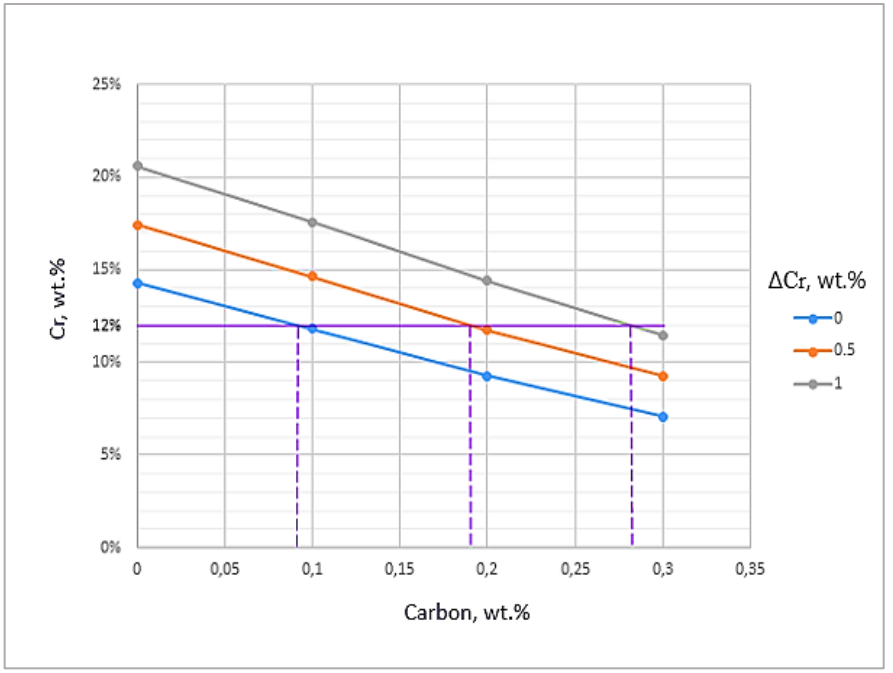

Fig. 15 - Mass fraction of unbound chromium (wt.%) versus on the amount of carbon impurity; **9,3 %** FIMA

The horizontal line of 12% marks the limit of passivity with respect to intergranular corrosion of austenitic steel. The dashed lines indicate the intersection of the 12% level with the dependences of the unbound Cr content on the amount of carbon impurity. These points characterize the concentration of carbon in the fuel to which the steel shell remains stable with respect to intergranular corrosion.

Conclusion

- The effect of unbound carbon on the steel cladding of a fuel element is most pronounced in the low-temperature part of the temperature range under consideration at maximum burn-ups and maximum concentrations of carbon and oxygen impurities, i.e. in the same areas of parameters at which the fraction of unbound carbon reaches its maximum values in the fuel.
- One of the possible ways to reduce the effect of carbon on the strength characteristics of steel claddings of fuel rods is to block its penetration into the shell.
- Detailed computational studies of the thermodynamics of the system “(U, Pu)N fuel with oxygen and carbon impurities + carbide-formers Cr + steel ChS68-ID” showed that the introduction of 1 wt.% Cr into the fuel should ensure the stability of the steel cladding with respect to intergranular corrosion.

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Thank you for your attention!