**“DEVELOPMENT OF CODES FOR CALCULATING THE CORROSION OF STEEL CLADDING OF FUEL ELEMENTS WITH MIXED NITRIDE FUEL, TAKING INTO ACCOUNT THE SEGREGATION OF IMPURITIES AT GRAIN BOUNDARIES”**

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 After reactor tests, the state of the claddings of the fuel elements made of EP823-Sh ferrite-martensitic steel noticeably differs from the state of the claddings made of the EK164 or ChS68-ID austenitic steels. In austenitic steels, as a rule, intergranular corrosion occurs. On the inner surface of EP823-Sh steel, pitting corrosion is observed. The typical depth of pitting corrosion is several tens of micrometers. At the same time, intergranular corrosion was not observed in ferritic-martensitic steels. Preliminary computational studies have shown that one of the reasons why ferritic-martensitic steels are less susceptible to intergranular corrosion compared to austenitic ones, despite the significantly lower average chromium content by volume, may be grain boundary segregation of alloy elements.

Therefore, in our opinion, it is necessary to conduct a detailed study and comparative analysis of the distribution of chromium, silicon, and other elements near grain boundaries in austenitic steels and near phase boundaries in ferritic-martensitic steels to describe the corrosion mechanisms in fuel elements with MNUP fuel. However, the computational code that allows the implementation of this study has not yet been created. There is also no corresponding database (DB) for calculating the segregation of impurities at incoherent boundaries in structural steels.

For example, the code for calculating the segregation of OpenIEC with the CALPHAD database considers only coherent grain boundaries and does not contain a block that takes into account the chemical interaction of steel components with impurities and fission products. Consequently, the solution of the problems of predicting the segregation of impurities in reactor materials cannot be realized at present. In addition, in Russia there are no calculation tools that allow analyzing the kinetics of intergranular and pitting corrosion of steels.

The problem of determining the equilibrium chemical composition of a multicomponent multiphase system, taking into account the redistribution of components along the boundaries, is a very difficult problem. However, due to the noticeable difference in the binding energies of most chemical compounds and the energies of grain boundary segregation, the problem can be divided into two minimization problems - the inner and outer cycle.

The task of the inner cycle is to calculate the thermodynamic equilibrium of the system under consideration with the determination of the concentrations of the components unbound into chemical compounds. This problem is solved by minimizing the Gibbs energy, taking into account the chemical bonds of the components of the system.

A complete set of necessary parameters for each individual substance in the database includes: chemical formula of the substance with integer stoichiometric coefficients indicating the phase state of the substance; coefficients of the approximating polynomial for the reduced Gibbs energy *ϕi* (*i*=1,2,…,7) [2]

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| --- | --- |
|  , | (1)  |

where *x*=T.10-4; *T* is temperature, K; the standard heat of formation of the substance *ΔH0f298* and the standard enthalpy change *H0298 - H00*. To determine the coefficients of the polynomial *ϕi* data on the temperature dependence of the heat capacity of the substance *Cp(T)*, as well as the standard values of the heat capacity *С0р298*, entropy *S0298* and changes in enthalpy *H0298 - H00* are used.

 The settlement system is then redefined. All chemically bound compounds are excluded from the calculation system, and only unbound elements remain, for which the problem of redistribution of components is solved taking into account grain boundaries and interphase boundaries, i.e. grain boundary segregation problem. This task is implemented in the outer cycle.

We used a physical and mathematical model of segregation based on the Langmuir – Maclean approach [3]. The segregation process was considered as the transition of atoms of a certain chemical element (I) from the bulk phase (b) to the boundary (s) with the replacement of the matrix element M (in our case, it is iron). Such a process can be written for any two-component system in the form of a "chemical" reaction:

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| --- | --- |
|  | (2) |

The condition for chemical equilibrium is the equality to zero of the total Gibbs energy of this reaction, i.e.

|  |  |
| --- | --- |
|  | (3) |

Data on the segregation energy of elements can be obtained by using quantum chemical calculations. The concentration dependences of the chemical potential of the *i*-th component in the bulk phase and in the surface layer are as follows:

|  |  |
| --- | --- |
|  | (4) |

where and are standard chemical potentials; and are the activities of the *i*-th component in the bulk phase and in the surface layer, respectively.

Taking these expressions into account, the chemical equilibrium condition will be written as

|  |  |
| --- | --- |
|  | (5) |

where is the standard Gibbs segregation energy element I to the boundary of the phase formed by M. Data on the segregation energies of elements can be obtained by using quantum chemical calculations or taken from experiment [4].

 In 2019-2020, we have developed prototype version of the program code for calculating the thermodynamics of austenitic and ferritic-martensitic steels, taking into account the segregation of elements at grain and interphase boundaries. The program code consists of an internal cycle based on the code "Program for calculating the equilibrium composition of austenitic and ferritic-martensitic steels", an external cycle - a computational code for the segregation of elements at grain boundaries and a database.

Using the developed prototype of the computational code, it was shown that the concentrations of the components that segregate at the grain boundaries can reach very high values. In this case, the approximation of “weak solutions”, which was used in the developed code to construct the configuration contribution to the entropy of the boundary subsystem, turns out to be not entirely correct. In this regard, when finalizing the code under consideration, it is necessary to refine the physical and mathematical model in terms of constructing a configuration contribution to entropy.

In the near future, it is planned to complete the development of this code, combining into one program the internal cycle - based on the code "Program for calculating the equilibrium composition of austenitic and ferritic-martensitic steels", the external cycle - a modernized code for calculating the segregation of elements at grain boundaries and phase boundaries and a database for calculating the segregation of impurities and components of steel.

An important task associated with the problem of calculating the composition of grain boundaries in multicomponent alloys is the expansion of the database on the parameters that are necessary for calculating the segregation of impurities at grain boundaries. First of all, this is the construction of the grain boundary distribution function within the selected classification for specific steels. Directly adjacent to this are the problems of restructuring the boundaries under the action of reactor radiation - radiation recrystallization and radiation-induced segregation. The problems of boundary rearrangement under the influence of temperature - temperature recrystallization - should also be investigated. It should be noted that quantum-mechanical calculations were carried out to expand the currently available database on segregation energies at grain boundaries.

The next stage is the development of codes for calculating intergranular and pitting corrosion, taking into account the segregation of impurities at grain boundaries. To simulate corrosion processes in steels, it is extremely important to take into account the structure of grain boundaries and their composition. On the basis of the created physical and mathematical model, will be developed a prototype of a program code for calculating the process of intergranular corrosion in austenitic steels, taking into account the structure of grain boundaries and their composition. Next, a demo version of the program code for calculating the pitting corrosion process in ferritic-martensitic steels, taking into account the composition of grain boundaries and interphase boundaries will be developed.

References

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