THE ISSUE OF NOVEL TRENDS IN FUEL ALLOYING TO REDUCE INTERACTION

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ABSTRACT

In the framework of the high density UMo fuel development, several solutions to U-Mo alloying are worldwide studied. A modification of U-Mo fuel alloying has been elaborated. It consists of formation of multiphase structure, viz., basic gamma U-Mo and ceramic or intermetallic phases (30-60% by volume). These phases shall have the maximal density of uranium, low molybdenum content, be well compatible with aluminium, highly irradiation resistant and precipitate along grain boundaries. The latter condition allows fuel particle production via grinding. After grinding the weakly interacting with Al ceramic phases are primarily available at the fuel particle surfaces, form some kind of protection barrier. Currently several systems are under consideration: U-Mo-Si, U-Mo-O, U-Mo-C, U-Mo-C-N-O-Si. The first results of developments are presented.

1. Introduction

For the past years the focus of the fuels area in the frame of RERTR program has been the development of aluminium-based dispersion fuels with high uranium densities [1]. Numerous experiments in this area of scientific exploration showed the U-Mo alloys, particularly U-10Mo, are the best candidates [2].
Currently the interaction between U-Mo fuel and Al is the basic factor that limits the serviceability of fuel elements. The interaction results in extra swelling of fuels, disappearance of a heat conducting matrix, a temperature rise in the fuel element centre, penetration porosity and so on [3, 4]. Presently the basic ways of resolving this problem have been contemplated. They are alloying of fuel, alloying of a matrix, creating protective barriers, application of monolithic UMo fuel [5, 6].
In terms of technology fuel alloying is the most optimal version since the process of fuel fabrication becomes complicated to a less extent. This paper deals with qualitatively novel approaches to fuel alloying that might help to resolve the interaction problem.

2. Problems of high density fuel application

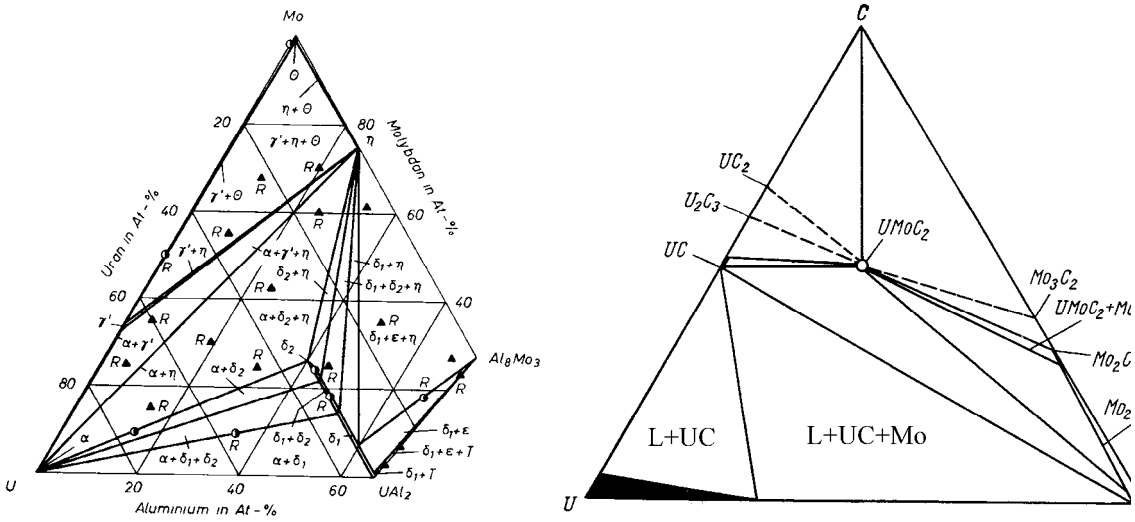
Transition from HEU to LEU in research reactors in the frame of RERTR Program were carried out gradually, starting from UAl_x fuel, then UO_2 and finally U_3Si_2. More effective is application of U-Mo (7-10% Mo) alloys having nearly 50% and 35% higher uranium density than UO_2 and U_3Si_2 accordingly. A huge amount of experience in this scientific area was achieved, including numerous irradiation tests, led to success. But still some disadvantages prevent widespread application of this type of fuel. Mainly they are:

- impossibly to produce fuel particles via grinding using standard fabricating plant equipment due to high ductility of U-Mo alloys – one need to use centrifugal spraying technology (atomization);
- low compatibility with Al matrix, especially at high burn-ups and heat flows;
- high molybdenum content worsen neutron-physical characteristics of reactor [7].

Therefore additional innovations were proposed, particularly, protective coatings, Al matrix alloying, usage of monolithic fuel, etc to diminish some of these drawbacks.

3. Novel concept of fuel alloying

As it was mentioned above, alloying fuel, particularly of U-Mo type, is one of the optimal ways to improve properties of fuel elements. Tradition approach to U-Mo alloying by using such elements as Nb, Zr, Ti, Al, Cr, Si, Sn, Re, etc individually or in various combinations not essentially decrease the interaction with aluminium as in used quantities all of them are included into γ-(U-Mo) phase solid solution [8]. Other drawbacks peculiar to all U-Mo alloys – high ductility, low radiation resistance and high Mo content – also characteristic of traditionally alloyed U-Mo alloys. Therefore, if we want really improve properties of U-Mo alloys we should use qualitatively novel approach. It consists of formation of multiphase structure, viz., basic gamma (U-Mo) and ceramic or intermetallic phases (30-60% by volume). These phases shall have the maximal density of uranium, low molybdenum content, be well compatible with aluminium, highly irradiation resistant and precipitate along grain boundaries. The latter condition allows fuel particle production via grinding. After grinding the weakly interacting with Al ceramic phases are primarily available at the fuel particle surfaces, form some kind of protection barrier.
As a rule, the alloying of UMo alloy with elements that form intermetallic compounds with uranium leads to the undesirable type of the phase diagram with ternary intermetallic phases that comprise molybdenum, e.g., U-Mo-Al, etc systems (see Fig. 1a) [9]. For molybdenum not to enter an intermetallic phase but to remain in a solid solution with uranium the type of the phase diagram (Fig. 1b) has to be realized when the phase triangle is restricted by U-U_2Mo-UX phases where UX is a binary intermetallic compound of uranium and an alloying element. This version is feasible in the U-Mo-C system (Fig. 1b) in which theoretically ternary compounds must not form close to the uranium angle of the phase diagram.



a **b**

Fig 1. Types of phase diagrams of UMo alloy with elements that form intermetallic compounds with uranium, a – system with ternary compounds (U-Mo-Al) [9], b – isothermal section of U-Mo-C phase diagram at 1500 °C

3.1 Study of U-Mo-Si system

At the first stage we start investigations of alloys in U-Mo-Si system as CALHAD modelling and Thermo-Calc Application Software showed that ternary U-M-Si compounds should not exist near uranium angle of state diagram; hence Si as a doping element to U-Mo would

satisfy above mentioned requirements. We chose alloys compositions near U-Si eutectic point as eutectics has special thermodynamic properties providing strong interatomic bonds and phase stability [10]. And our predictions were partly confirmed experimentally [8, 11].
Therefore, using a casting method a group of alloys were fabricated with additives of Si in the range of eutectic point (0.5 – 1.5%) as well as Si + Al (1.2% in total) and low Mo contents within 5 to 6.5 % were produced and then examined metallographically. The microstructures of some alloys are shown in Fig. 2.

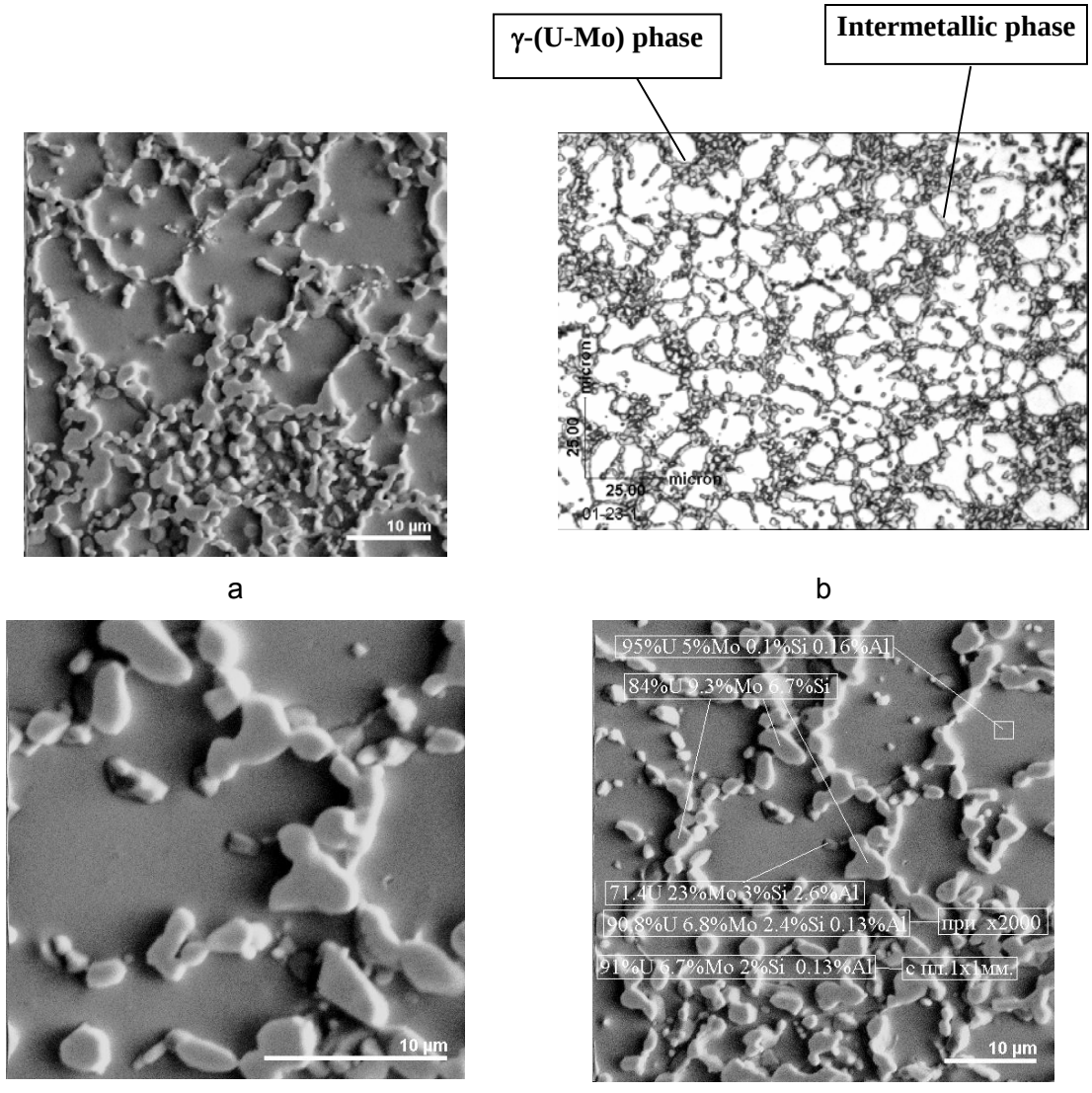
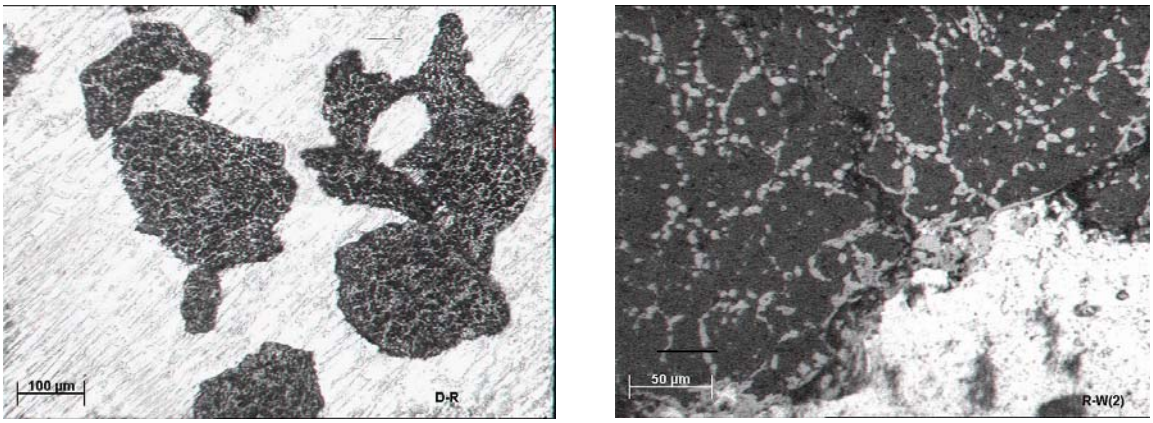


Fig 2. Structures of alloyed UMo multiphase alloy; a, b – U + 5.7Mo + 1.04Si;
c, d – U + 6.3Mo + 0.9Si + 0.15Al

After casting some alloys were annealed at 500^0C for 4 hours to study stability of γ(U-Mo) phase. Microstructures of two alloys (U+5.7%Mo+1.04%Si – weight percent) as well as (U+6.3%Mo+0.9%Si+0.15%Al) are shown in the Fig. 1. It consist mainly of 2 phases: γ(U-Mo) phase containing 5% of Mo and 0.1% of Si and intermetallic ternary phase U-9.3Mo-6.7Si, probably $(UMo)_3Si_2$. It should be mentioned that gamma phase did not decompose after annealing in spite of low molybdenum content.
The main challenge in alloying UMo fuel is a decrease in the γ(U-Mo) phase stability at the expense of a reduced molybdenum content when alloying elements, specifically, aluminium are added. The same effect in less extent takes place when alloying with silicon that contradicts with thermodynamic calculations. Some molybdenum leaves the gamma uranium phase for the intermetallic phase, depleting in this way the gamma solid solution in Mo, which

shall decrease its stability. As it might be seen from Fig. 2d molybdenum is present in the intermetallic phase of uranium with silicon which is undesirable.
But in our case gamma (U-Mo) phase stabilization occurred at relatively low concentration of Mo in gamma uranium phase. This effect can be explained by stabilizing acting of elements at the second phase through their mutual grain boundary [10, 11]. This is a very interesting effect, confirming our approaches of existing so called “interphase metallic bond” in multiphase systems, opens the possibility of gamma phase stabilization using limited quantities of alloying elements and refers to fundamental aspects of metal science.
After grinding the weakly interacting with Al intermetallic phase is primarily available at the fuel particle surfaces, forming some kind of a protection barrier. Figure 3 (a, b) illustrates structures of fuel compositions with Al matrix in the original condition and after anneal at 600^0C for 6 hours. Fuel was prepared via grinding. It is well seen from Fig. 3b that the intermetallic phase weakly interacting with aluminium is primarily available at the fuel particle surfaces, that is why the interaction is of a nodular mode. The acquired results indicate the feasibility of diminishing the interaction through this method.



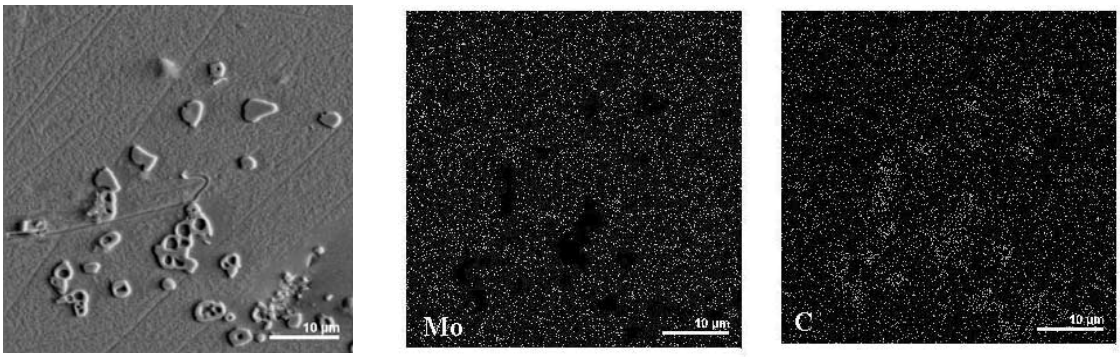
a b

Fig 3. Microstructure of fabricated fuel composition with UMo alloy, a – (U + 5.7Mo + 1.04Si)/Al as fabricated; b – (U + 6.3Mo + 0.9Si + 0.15Al)/Al - 6 hours annealed at 600 °C

Further developments on U-Mo-Si system alloys should be directed on investigation of the following effects:
1. Determination the lowest content of Mo to retain gamma phase stability.
2. To increase Si content with simultaneously decreasing of Mo to decrease neutron capture as well as alloy ductility.
3. To use annealing for more promising U_3Si instead of $(U,Mo)_3Si_2$ formation in order to remain Mo in gamma phase as well as determination of Mo/Si optimal ratio in case of annealing.

3.2. Consideration of U-Mo-C, U-Mo-O, U-Mo-(C, O, N, Si) system

As it was mentioned in chapter 3 carbon should satisfy novel concept fully (Fig. 1b) [8]. We also assumed, that except carbon it may be nitrogen and oxygen as they are soluble in UC, therefore, can form complex U(N,C,O) composition, to be in thermodynamic equilibrium with U-Mo gamma phase. Small silicon additions can be also added to this composition. Our predictions were based on our previous works [8, 11]. The confirmation of this might be seen in Fig. 4 that illustrates the distribution of the elements in the U-6.5Mo alloy with a carbon impurity in the characteristic radiation of U, Mo and C. The unavailability of molybdenum in carbide phase is clearly seen in carbon phase inclusions along the grain boundaries of the γ-solid solution of U-Mo was demonstrated.
The similar approach we implement in developing high density accident tolerant fuel for PWR. It is based on U-Mo alloy with multicomponent doping forming metalceramic structure [12].



a b c

Fig 4. Distribution of elements of U-6.5Mo alloy with carbon impurity in characteristic X-ray radiation: a – secondary electrons, b – Mo, c - C

Our first experiments with doping some of these elements to U-Mo based alloy confirmed our assumption. Alloys based on U-Mo and 0.5%C and 1.0%O additions relatively, were fabricated by arc-melting. Ingots and microstructures are shown in Fig. 5 and Fig. 6.

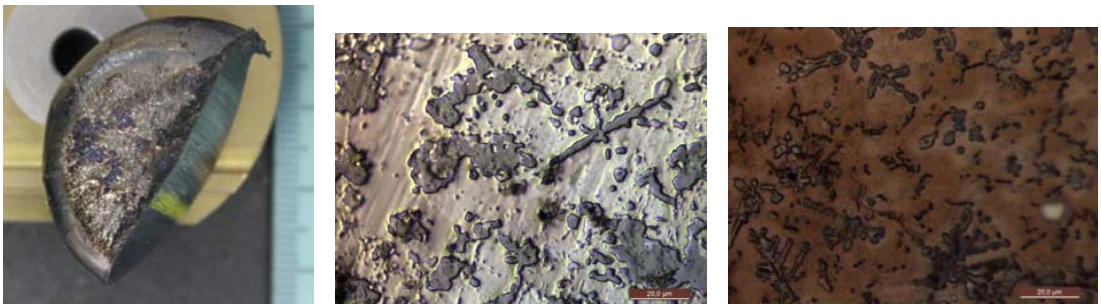


Fig 5. Ingot and microstructure of U-Mo-0.5%C

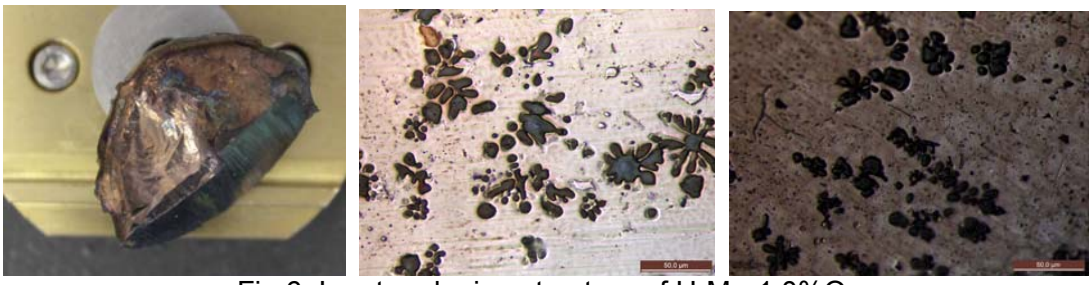


Fig 6. Ingot and microstructure of U-Mo-1.0%O

Preliminary investigations showed the availability of the main two phases in the structures – gamma phase and uranium carbide in the first alloy and gamma phase and dioxide uranium in the second alloy.

Second step was to go further and try to modify this system using multicomponent doping. It should be mentioned that the idea to implement so much doping elements in U-Mo alloy based on the experimentally validated effects in so-called High Entropy Alloys (HEA) [13]. It appears in interatomic bond strengthening by so-called “entropy force”, the nature of which is not clear yet. Its value depends on the value of configurational entropy (the more doping elements – the better). Our analysis revealed the mechanism of this phenomenon, which closely connected with energy sense of configurational (mixing) entropy [14].

To start multicomponent doping we firstly made consideration of possible properties of the second phases (the primary retains U-Mo gamma phase). Table 1 illustrates the possible secondary phases formation additional to main gamma-phase and their uranium densities. The latter is important to estimate the final properties of so-called metal-ceramic alloys with different volume fraction of the main U-Mo gamma phase, which in any case, determine the uranium density of alloys [12].

	Phase density in alloy	Phase uranium density
Main U-Mo gamma phase, 60%	17-18	16-16,9
Secondary phases:		
UO_2	10,96	9,7
UO (in case of stabilization by C and O)	13,63	12,8
UC	13,6	12,9
UN	14,3	13,5
U(C,N,O,Si)	13,7	13
U_3Si_2	12,2	11,3
U_3Si	15,6	14,6

Tab 1: Some properties of the main and secondary phases in the multicomponent doped U-Mo alloy

Several alloys based on U-Mo-C-O-Si and U-Mo-C-O were then fabricated by arc-melting. Ingots and microstructures are shown in Fig. 7.
More complicated structures appeared in these alloys. The structure of one of the U-Mo-(C,O,Si) is illustrated in Fig. 7. The most important result is the availability of the main gamma uranium phase in spite of low content of molybdenum in an alloy.

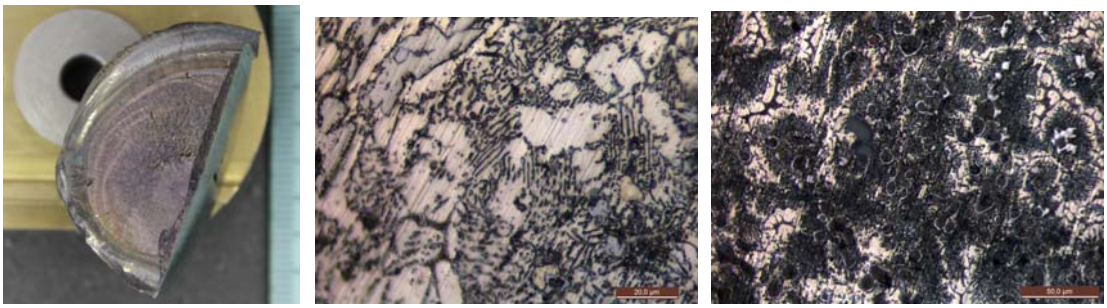


Fig 7. Ingot and microstructure of U-Mo-(C-O-Si)

Investigation in the direction of multicomponent doping of U-Mo are at the first stage and will be continued as they are partly coincide with the development of ATF Russian Program [12].

3.3. Advantages of metal-ceramic alloys

Commercial advantages for application in research reactors in comparison with U-10Mo fuel:
- simplification of the technology for fuel particles manufacturing on standard plant equipment (no need to use centrifugal spraying);
- improvement of compatibility of fuel with aluminum matrix and, as a result, increase of its serviceability;
- reduction of the molybdenum content in the alloy, which improves the neutron-physical characteristics of the reactor;
- reducing the swelling of the fuel due to the presence of radiation-resistant ceramic phases in its structure;
- increase in fuel burn-up to 60-80 at% due to increased uranium capacity and radiation resistance;
- the possibility of using low-enriched fuel in high-flow research reactors.

5. Conclusion

Potentialities of U-Mo fuel alloying to reduce interaction have been analyzed. In the framework of the high density UMo fuel development several solutions to U-Mo alloying are worldwide studied.

A modification of U-Mo fuel alloying has been elaborated. It consists of formation of multiphase structure, viz., basic gamma (U-Mo) and ceramic or intermetallic phases (30-60% by volume). These phases shall have the maximal density of uranium, low molybdenum content, be well compatible with aluminium, highly irradiation resistant and precipitate along grain boundaries. The latter condition allows fuel particle production via grinding. After grinding the weakly interacting with Al ceramic phases are primarily available at the fuel particle surfaces, form some kind of protection barrier. The optimal doping elements to U-Mo were calculated.
Principally novel results were received for stabilizing gamma U-Mo phase with low molybdenum (5%) content in eutectic type alloys by the third neutral stabilizing element. It can be explained by additional stabilizing impact of Mo located not only in gamma (U-Mo) phase, but also in the secondary intermetallic phase.
Currently several systems are under consideration: U-Mo-Si, U-Mo-O, U-Mo-C, U-Mo-C-N-O-Si. The first results of developments are presented.

References

1. G.L. Hofman, M.R. Finlay, Y.S. Kim, H.J. Rue and J. Rest "Observations of the Nucleation and Evolution of Porosity in U-Mo Fuels", Proc. 2005 International Meeting on Reduced Enrichment for Research and Test Reactor, Nov. 6-11, 2005, Boston, USA.
2. F.Huet, B. Guidon, P. Lemoine, C Jarousse, F. Wijtsma, G. Dassel, G. Hofman, J. Snelgrove " The UMUS Failure : Facts and Analyses ", Proc. 2003 International Meeting on Reduced Enrichment for Research and Test Reactor, Oct. 5-10, 2003, Chicago, USA
3. G.L. Hofman, Y. S. Kim, H.J. Rue, M.R. Finlay, D.W. Washs "Improved irradiation behavior of uraniummolybdenum/aluminum dispersion fuel", Proceedings of the Research Reactor Fuel Management (RRFM-2007) Conference, Lion, France, 11.03-14.03.2007, available through the European Nuclear Society (ENS) website.
4. C.R.Clark, G.A. Moore, J.F. Jue, D.E. Burkes, T.C. Wiencek "Update on US high density fuel fabrication development, Proceedings of the Research Reactor Fuel Management (RRFM-2007) Conference, Lion, France, 11.03-14.03.2007, available through the European Nuclear Society (ENS) website.
5. "Post irradiation examination of monolithic mini-fuel plates for RERTR-6&7", Proceedings of the Research Reactor Fuel Management (RRFM-2007) Conference, Lion, France, 11.03-14.03.2007, available through the European Nuclear Society (ENS) website.
6. Yeon Soo Kim, G.L. Hofman, J.S. Cheon, A.B. Robinson, D.M. Wachs, J. Nucl. Mater. 437 (2013) 37.
7. Gilles Youinou, R. Sonat Sen, Enhanced Accident Tolerant Fuels for LWRs – A Preliminary System Analysis, INL/EXT-12-30211, FCRD-FCO-2013-000359, INL-DOE, 2013.
8. A. Savchenko et al. Novel Trends in Fuel and Matrix Alloying to Reduce Interaction, Proceedings of the Research Reactor Fuel Management (RRFM-2007) Conference, Lion, France, 11.03-14.03.2007, available through the European Nuclear Society (ENS) website.
9. G. Petzow, J. Rexer, Z. Metallkd. 62 (1971) 34-38.
10. A. Savchenko, Entropy effects in multiphase systems. Mechanism of eutectics melting. J. Atomic Strategy, S-Petersburg, Issue 111, February 2016, 28-33, available online http://www.proatom.ru.
11. A. Savchenko, Conceptual study of multiphase structure of high uranium density alloys to reduce chemical interaction, Proceedings of the 45èmes Journées des Actinides (JDA-2014) Conference, Ein-Gedi, Israel, 15.05-20.05.2014, 158-159.
12. A. Savchenko, Brief Review of A.A. Bochvar Institute Activities in ATF Developments, OECD/NEA Expert Group, in Proceedings of Fifth EGATFL Meeting, 11-15 April, 2016, Paris, France.
13. 5. A. D. Wissner-Gross, C. E. Freer, Causal entropic forces. Phys. Rev. Lett. 2013, 110, 168702–5.
14. A. A. Savchenko. Entropy effects in real systems. J. Atomic Strategy, S-Petersburg, Issue 110, January, 2016, 14-19, available online http://www.proatom.ru.