Lithium in nuclear and thermonuclear power engineering

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Abstract. The information about requirements to lithium as a coolant and working medium of the IFMIF neutron target is given. Some research results relating to purification of lithium from impurities and determination of their concentration, which demonstrate possibilities of fulfilling the IFMIF requirements, are presented.

1. Introduction
This metal, which has the lowest density, the highest thermal capacity, and the highest evaporation heat, has no equal one with respect to ability of heat transfer, i.e. to be a coolant. However, choice of the coolant is determined not only by its thermophysical properties, but by a number of other properties as well. Therefore, field of application of every coolant is limited. In powerful nuclear fast reactors sodium turned out preferable.

At present, lithium is considered as a promising coolant for high temperature space nuclear power systems with operation temperature of 1000°C and more. A great positive experience of ground tests is gained of circulation loops with lithium, whose structural materials are refractory metals (niobium, molybdenum and tungsten) and their alloys. But density of the refractory metals exceeds stainless steel one by a factor of 1.5-2, therefore use of light coolant gives no advantage. It seems that using lithium will be necessary in nuclear power systems with electric power of 100kW and higher.

The authors of this report think that lithium can be used in space systems of less power with thermoionic conversion of energy too. Heat abstraction from thermoionic converter anodes in the known space nuclear systems BUK and TOPAZ was made by means of sodium-potassium eutectic alloy. The alloy temperature in the circulation loop was 500-600°C. At this temperature both lithium and sodium-potassium alloy can be used in stainless steel loop. It will permit to reduce piping diameter and mass by a factor of 1.7. The loop volume (and coolant one) will decrease by a factor of 3. All this will give sufficient economy of mass of heat removal system.

Replacement of the loop stainless steel by vanadium alloy with 4% of chromium and 4% of titanium seems even more attractive. This alloy is considered now as a possible structural material for lithium circulation loops of thermonuclear systems. It is noticeably lighter than steel, has sufficient heat resistivity, and is reduced activated under reactor conditions. It is expected that the alloy compatibility with lithium is good enough, but there is no yet operating experience of vanadium loops with lithium. It seems that the lightest power system can be created on the base of vanadium alloy as a structural material and lithium as a coolant.

The vanadium alloy is supposed to be used in the project of Russian test blanket module for international thermonuclear reactor ITER, as well as in future Russian demonstration thermonuclear
reactor DEMO. Therefore, investigation of thermodynamic and physical-chemical properties of vanadium alloy-lithium-nitrogen-oxygen-carbon system is necessary to develop technology of lithium application as a coolant in nuclear and thermonuclear systems.

But some other structural materials – austenitic and reduced activated ferrite-martensitic steels – are also considered, in order to use them in thermonuclear systems. In particular, these steels are supposed to be used in the international project of neutron source for irradiation of structural materials – IFMIF (International Fusion Materials Irradiation Facility). Therefore it is also necessary to study lithium physical and chemical interaction with impurities in steel loops.

In 2002-2006 the ISTS project #2036 “The thermal-hydraulic and technological investigations for validation of the project of lithium circulation loop and neutron lithium target for IFMIF” was carried out in the IPPE. One of the main points in the project was research of hydrodynamics of a flat lithium jet in a curvilinear channel with a rectangular cross section. It is the lithium jet that is the target irradiated by 32MeV deuterium ions. As a result of nuclear reaction of deuterium with lithium, neutrons with energy of 14MeV are generated [1]. Lithium jet flows in vacuum at the velocity up to 20m/s, inlet/outlet temperature is 250/285°C. In interacting, 10 MW of heat is evolved in the irradiated lithium volume with deuterium ion beam. High lithium purity demands: content of the above-mentioned impurities should not exceed 10ppm [1]. Therefore purification of both lithium and circulation loop from impurities and determination of impurity concentration was the second important point of the investigation.

To carry out the ISTC Project three experimental lithium plants were constructed in the IPPE. Lithium Test Facility (LTF-M) was intended for investigation of the target hydrodynamics. Lithium inventory is 280 liters, flow rate is 50m³/h, and the facility height is 15m. The second plant – LTF (about 100 liters, 10m³/h) – was intended for lithium technology investigations. The third facility was “the plant with Rotating Disc” (RD) – for material science researches.

Some results are given in this report relating only to the second point, which seems to be closer to the conference topics. These are some information about lithium purification and determination of impurity concentration in it.

2. Purification of lithium
The first stage of lithium purification before filling it into the above test facilities was settling melt lithium in dump tank at the temperature of 210-230°C during 8-24 hours. After that, lithium was pressed out from the tank into the loop by argon or helium pressure. It may be considered that concentration of impurities corresponded to saturated condition at this temperature according to equations of solubility:

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\begin{align*}
\lg c_O &= 6.992 - 2896/T, \text{ppm} \\
\lg c_H &= 6.678 - 2308/T, \text{ppm} \\
\lg c_N &= 7.57 - 2080/T, \text{ppm}.
\end{align*}
\]

Further purification was performed by means of cold traps: usual three-zone (cooling and crystallization, sedimentation, filtration) and diffusive disc ones [2]. Minimal temperature of lithium at the cold trap output was 193°C. In accordance with the above equations, oxygen concentration should be 6ppm, hydrogen one – 54ppm, nitrogen – 1275ppm. One can see that concentration less than 10ppm required by the IFMIF can be achieved by means of cold trap only for oxygen, but other methods of purification from hydrogen and nitrogen are needed, in particular getter traps. But these traps require high temperature – 600-700°C, and that badly combines with low temperature facility IFMIF, where maximal temperature is 285°C.

As nitrogen is the most dangerous impurity in respect of corrosion and has the greatest concentration, maximal attention was devoted to purification from it. The getter dissolving in lithium – aluminum – was used [3]. Aluminum dissolves well in lithium even at low temperature, and purification can be performed at the temperature of 250-300°C, that corresponds to the IFMIF operating temperature.
Purification of circulating lithium from nitrogen by aluminum was investigated at the RD facility. The plug indicator was used to detect impurities. Plugging temperature was \(~ 300^\circ\text{C}\) before purification. Then 0.9\% at.Al was embedded into lithium. The plugging temperature was measured once more after embedding aluminum. It turned out \(~ 190^\circ\text{C}\). Further chemical analysis of the lithium sample showed nitrogen concentration of 1.6 – 6.0ppm. Thus, the required purification of lithium from nitrogen can be achieved, but it is necessary to remove aluminum nitride from the loop, for example, by means of filter or by settling it in the tank. Such purification was carried out at the RD facility as well.

As for purification of lithium from hydrogen, development of effective method is still urgent.

3. Monitoring impurities in lithium

Determination of oxygen content in alkali metals is traditionally performed by means of sampler-distiller [2]. The method sensibility is $2 \cdot 10^{-4}$ \% mass, accuracy \pm 7\%. But this method has a number of demerits, one of which is impossibility of continuous monitoring. As for lithium, an additional demerit is high temperature of distillation – 750\°C. In the Institute for Physics and Power Engineering, the authors of this work have a great enough experience of determination of oxygen concentration in sodium and in sodium-potassium alloy by means of electrochemical cell with a solid electrolyte on the base of zirconium dioxide stabilized by yttrium dioxide [3]. This method is used for the present only at experimental facilities. Stability of this electrolyte in lithium is less than in sodium, at the temperature exceeding 300\°C it dissociates and decomposes, but at the IFMIF working temperature of 250-285\°C it can work for some time, and the authors of the report used it.

The electrochemical cell with reference electrode of indium saturated with oxygen was installed at the RD facility. Measuring EMF was carried out in lithium flow immediately after filling the loop. Temperature of lithium flowing through the electrochemical cell was changed in the range of 181-320\°C to obtain EMF as a function of temperature. Then the same measuring was carried out in immovable lithium, i.e. under quasi-equilibrium conditions. The data received are shown in Fig. 1. At heating from 200\°C to 240\°C, the cell EMF changed along line 1. The line slope \(\frac{\partial E}{\partial T}\) corresponds to oxygen isoconcentration \(~ 20\text{ppm}\). At further heating EMF changed along line 2. It is because wetting steel by lithium, dissolving oxide films on steel, and increasing oxygen concentration in lithium began, probably, at 240\°C.

In Figure 1 one can see that curve 2 coincides with saturation line of lithium by oxygen at the temperature of about 300\°C (87ppm). Perhaps, just this content of oxygen was in lithium after dissolving oxide films on steel surface before purification of lithium by the cold trap. Then, after purification of lithium by the cold trap of the RD facility minimal oxygen concentration falls down to \(~ 10\text{ppm}\) (the most left point on curve 3).

Another method used by the authors for monitoring impurities is the method of plug indicator [3]. This is simple and quick enough method, and the device can be automatically operating and to give information on-line. In order to decrease time lag and to increase sensitivity of the device, new design was developed, which is shown in Figure 2.

In this device the orifice to be plugged is formed as a narrow annular gap between a movable plunger 1 and casing of magnetic flow meter 5, and the flow meter electrodes are combined with thermocouples measuring lithium temperature. When the plunger is in lower position, the gap is 0.5mm, i.e. approximately the same as in the reference device. When the plunger is in upper position, the gap is \(~ 1\text{mm}\). So it is possible to get high enough lithium velocity (and the flow meter sensitivity) even at low flow rate. Therefore the power necessary to cool lithium is also low.
Figure 1. Electrochemical cell EMF as a function of lithium temperature

The diagram of flow rate through the indicator versus temperature of lithium during its decreasing is shown in Figure 3. There are three temperature values, at which decrease of flow rate occurs, i.e. three “plugging temperatures”: 300, 220, and 212°C. It is possible to suppose that maximal temperature relates to nitrogen because cold traps do not catch it, and, hence, its concentration should be highest. Minimal temperature, probably, relates to oxygen, and middle one – to hydrogen. If so, nitrogen concentration was 8700ppm, hydrogen one – 83ppm, and oxygen – 14ppm.

Heating the indicator was begun at 212°C, and dissolution of impurities was achieved at the temperature of 295°C, close to plugging temperature.

After four hours of the cold disc trap operation, plugging diagram was obtained again. It is presented in Figure 4 by a black color. The first plugging is noted at the temperature of about 295°C, the second – at the temperature of about 190°C, and dissolution – at the temperature of 210°C. Conservation of the first plugging temperature as 295°C indicates that it is caused by nitrogen indeed as it is known that the cold trap badly catches nitrogen. Decrease of the second plugging temperature from 220 to 190°C indicates that the trap diminished oxygen and hydrogen content in lithium.

Then aluminum was embedded in lithium. The diagram of plugging is shown in Figure 4 (curve 2). One can see that the indicator fixes single temperature of plugging equal approximately to 190°C. This indicates that purification of lithium from oxygen took place, and plugging was caused by impurities of oxygen and/or hydrogen. Corresponding concentrations of impurities are at most: oxygen – 5.5ppm, and hydrogen – 50ppm. Simultaneously lithium sample was taken, chemical analysis of which showed nitrogen content in lithium of 1.6 – 6 ppm.
Figure 3. Plugging diagram before purification. Li flow rate through plug indicator as a function of temperature

Figure 4. Plugging diagram after purification by cold trap (1) and aluminum (2)

4. Conclusion
The investigations performed showed possibility of achievement of required lithium purity for the IFMIF, at least from the most corrosively dangerous impurities of nitrogen and oxygen. Search of the most optimal method of purification from hydrogen should be else continued.

The plug indicators of impurities can be used for on-line monitoring lithium contamination at test facilities, and at corresponding embodiment – for the IFMIF as well. It is expedient to prolong the work on improving the plug indicator in order to ensure more accurate identification of impurities and to create device automatically operating in a nonstop regime.

References
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