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# Mechanical and Chemical Testing of Metallic and Elastic Parts of Gasket in an Environment of Fluoride Salts

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***Abstract*— This paper describes selection of individual components for sealing elements in environment of melted salts. Individual suitable nickel and non-nickel alloys along with flexible elements of the sealing (graphite foil, mica) are described. In conclusion are outlined individual experimental procedures for long-term testing of the selected components.**

***Keywords*—fluoride salts, gaskets, graphite, high temperature**

## I. Introduction

The melts of mineral salts are used in many industrial applications e.g. production of very volatile metals like lithium, sodium, rare earth metals, uranium, plutonium or electrolytic metal coating with titanium, tungsten, molybdenum etc. Another important field where melts of mineral salts can be used is the field of cooling media. The melts can be used as heat carrier for some types of reactors or selected salt compounds are used for reprocessing of used nuclear fuel.

An example of a nuclear reactor that is using fluorine salts as heat-carrying medium is Molten Salt Reactor MSR. This concept is classified, along with other five concepts of nuclear reactor, as generation IV nuclear reactor and it can be used as breeding or transmuting reactor. While in operation a breeding or generative salt mixture are considered for use. Furthermore, the reactor can be used for electricity or hydrogen production. This is due to its high operating temperature. Feasibility of such concept was verified in the last century in Oak Ridge National Laboratory in USA.

A candidate for carrying salt of the primary circuit for the MSR or for transport of high potential heat is LiF-BeF2 (melting point of LiF-BeF2 is ca. 729 K).

Alongside its favorable thermo-physical attributes [2], [6], [8] (specific heat Cp ≈ 2400 J/kgK at 973 K , thermal conductivity k ≈ 1 W/mK at 873 K) it also have a very low effective profile for neutron capture when isotope Li-7 is used in the mixture. Pure FLIBE is not particularly corrosive, however addition of oxidizers (e.g. UF4 in the case of fuel salt MSR ) rapidly increases its corrosive potential [1], [5]. A certain disadvantage of this salt is a difficult manipulation due to the presence of toxic beryllium and high cost of Li-7 separation. This is why is sometimes (particularly in the USA) preferred melt FLINAK in the experimental laboratory conditions [2],[9],[10]. However, FLIBE is still considered a reference melted salt for FHR and MSR.

Fluoride and its compounds are aggressive substances and strong reducing agents capable of combining with almost every element. This is why it is very important to know mutual interactions of specific medium with every construction material while building any device working with such compounds. Sealing elements are one of construction part of any device and their attributes almost always define operability, lifetime and safety of the device.

Experience from operation of many industrial and nuclear facilities shows that the most used and best sealing elements of flanged connections are combined gaskets. These are composed from at least two different materials. One usually is a “matrix” made of strong – metallic material and the other is flexible. While designing a combined gasket it is necessary to know the behavior of each material while interacting with each other and with the sealed medium as well.

## II. PROCEDURE

This flexible and metallic materials need to be tested for chemical and heat resistance, firmness and radiation resistance. Tested material samples are collected from available stock of each material i.e. panels, foils, loose stock etc. For objective reasons this article does not publish names of companies producing these stock. Testing procedures can be sorted as testing of compressibility mostly of the flexible materials, chemical resistance of the flexible and metallic materials and heat resistance.

### *A. Selection of tested flexible materials*

For the experiment were primary chosen two types of material. The first is expanded graphite and the second is mica. Further will be tested their combinations with a metallic material. The starting stock for the graphite testing will be: panels, loose expanded graphite and GERŽET graphite (graphite produced from plates by a special technology developed in MICo Company). The starting materials for mica testing will be plates and segments of foil.

Graphs of compressibility are supplied for some materials. But this is rare and due to their accuracy they are not very applicable in practice because the relevant data are supplied only as informational pamphlet from which it is not possible to deduce the data. Furthermore, such data are not accompanied with information under what circumstances they were measured.

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On the following Fig.1 is shown one testing sample from expanded graphite before the test (left) and after the test (right). The sample after the test is cut so the impact of the deformation on its structure and layering can be observed.

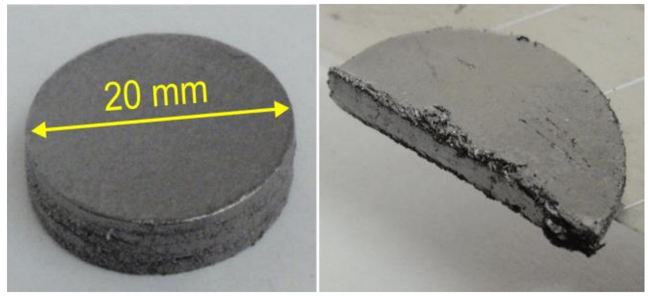


**Fig. 1. Graphite sample before testing (left), vertically sample cut (right)**

### *B. Selection of testing metallic materials*

*Nickel alloys*: Many years of material development in USA have shown that the best candidates for construction materials compatible with fluoride melts are nickel and alloys based on nickel doped with chrome and molybdenum that shows high temperature resistance up to 1023 K e.g. Inconel 718 and especially Hastelloy. During long time tests of natural and forced convection Hastelloy N has shown very low amount of material loss due to corrosion in different mixtures of fluoride salts in temperatures up to 1005 K. For example, in melted salt FLIBE of secondary circuit there was no corrosion damage on Hastelloy N after 26 000 hours [1].

Alloy Hastelloy N was directly created to be compatible with salts containing UF4. Chemical corrosion happens in warmer parts of the circuit due to selective oxidation of chrome and in colder parts of the circuit due to reduction and subsequent deposition of chrome. In higher concentration of fission products and greater neutron flow Hastelloy N shows only a small inclination for radioactive damage like helium embrittlement and embrittlement at grain boundaries. The research showed that the embrittlement is connected to tellurium and mostly tellurides presence at the grain boundaries that are in contact with salt. Tellurium is more active in creating bonds than fluoride and binds with chromium that then leaves the material structure. Modified Hastelloy N that solves this serious problem contains 1.5–2% of niobium that improves resistance against tears creation. Positive is also an addition of titanium or adjustment of redox potential of the salt so it keeps tellurium dissolved and denies it to infest Hastelloy N [1].

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In Kurchatov Institute in Moscow were investigated properties of experimentally created nickel alloy HN80MT and its modification HN80MTY [11]. Compared to the Hastelloy N this material shows greater corrosion resistance. Great corrosion resistance in static ampoule corrosion tests verified in independent laboratories at Kurchatov Institute also shows a Czech alloy MONICR developed in cooperation of ŠKODA JS PLC and COMTES FHT PLC. Hastelloy N and MONICR show, unlike the HN80MT, good weldability by electron beam and auxiliary materials under protective atmosphere [1], [12].

Next to corrosion speed in degradation are also important microstructural changes. Alloys with higher content of chromium are especially prone to intergranular corrosion. The smallest amount of this corrosion and chromium depletion showed Hastelloy N. Hastelloy X showed severe intergranular infestation. Incoloy 800H showed substantial pitting corrosion at the surface and intergranular corrosion in the whole depth of the sample. Inconel 617 showed intergranular corrosion with cavities filled with salt.

*Non-Nickel alloys:* Alternative materials to nickel alloys can be stainless steels that have higher resistance against radiation embrittlement, but their temperature limit is at 923 – 973 K. They contain less nickel, therefore there will not occur problem with helium bubbles generation. Helium embrittlement can be eliminated by precipitation of fine carbidic particles in matrix near grain boundaries. At them small bubbles of helium settle and because of the number and size of the carbidic particles the helium bubbles cannot grow in critical size for embrittlement.

When in contact with salts containing UF4 the stainless steels of ASTM 304L and 316L types, there occur the same corrosion mechanism of chromium extraction as with the MONICR, Hastelloy N and HN80MT. Due to much higher concentration of chromium in steel than in the said alloys the amount of extracted chromium is much greater. Circuit made of 304L after 9 years showed even corrosion loss 21.8 µm. But there were found undersurface cavities at exposed surfaces. Material 316L showed both said effects, but with little better absolute values. Russian Institute of Technical Physics proposes alternative austenitic steel with 12% of chromium, 18% of nickel and 10% of titanium and appropriate melted salts [1], [5].

In pure FLIBE were, besides austenitic (316L), also tested ferritic steels JFL-1. In static conditions at temperatures 773 – 873 K and duration of the test 2003 h both steel showed acceptable corrosion speeds for a construction material [1]. But that concerns assumption that over the whole duration of the test with no exception will be ensured reduction environment in the melt. In contrary, Hastelloy N in temperatures up to 970K does not require any control of its redox potential. Over 1020K there is not enough data for reliability projection [2].

## III. Compressibility Of Flexible Materials

The objective of experimental measurement is to find out exact deformation behaviour of flexible materials. The output of the measurement are graphs of deformation of flexible material in dependence on their density resp. volume. An important parameter for this measurement is compression of tested material. That means that for practical use will be defined three curves for graphs. The first will be dependence of compression of material (eS) to applied pressure (QS). The second curve will express dependence of the density of material (ρS) at applied pressure (QS) and the third curve will describe the dependence of density of material (ρS) at its immediate deformation (eS). In the course of the experiment are directly measured following values: Pressure of oil and movement of upper pressure cylinder i.e. deformation of gasket (eS). Next will be measured weight and proportions of samples, both prior and after test. Especially proportions and their time dependence after compression are important factor for determination of portion of elastic and plastic deformation of given material. This portion of both deformations in practice influences several attributes of the gasket at once. Especially so called settling, respective relaxation of the sealing and the value of back spring of the whole sealing. All these parameters are an important factor for development itself especially for combined gaskets. With these the effects are multiplied in dependence on combinations of individual flexible and metallic materials.

The whole measurement will take place at hydraulic press with minimal achievable force 240 kN. The head of the press will be equipped with device for exact measurement of the pressure force of the press.

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Movement of the device fixed in the press is 10 mm. Diameter of sample is 20 mm. Achievable pressure on the tested material is 600 MPa.

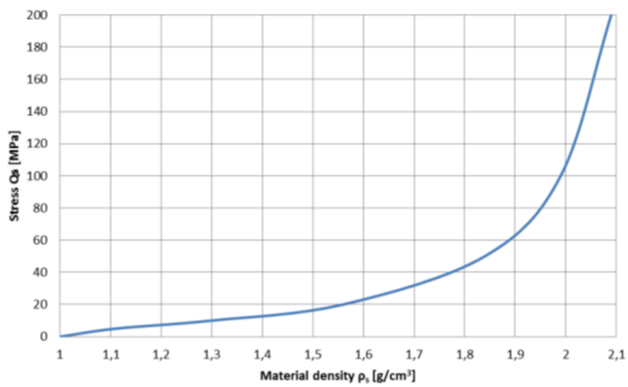


**Fig. 2. Graphite sample before testing (left), vertically sample cut (right)**

The graph in Fig. 2 is composed of available data from one of the manufacturer of the graphite plates. Based on the performed tests, these data will be optimized.

The measurement is performed at the ambient temperature 300 K. Next, the measurement of the same properties will take place under elevated temperatures, i.e. 423 K, 523 K, 623 K, and 723 K due to the normative requirements of EN 13555 with the permitted increase temperature max 2K/min.

## IV. EXPERIMENT

### C. *Preparation of testing ampule LiF-BeF$_2$*

As most suitable mixture composition seemed to be LiF-BeF$_2$ with composition [(66 mol. % LiF – 34 mol. % BeF$_2$) ~ (51.72 w. % LiF – 48.28 w. % BeF$_2$)] that is proposed as reference mixture for primary (respectively fuel) circuit of FHR and MSR. The melting temperature of the mixture is approximately 732 K. After accurate weighting and mixing of individual fluorides the mixture was placed in a melting pot. The mixture was melted in regulated furnace that distinctly exceeds the melting temperature of the mixture. The melted mixture was then cooled approximately three hours in graphite pots. After three hours we extracted the gags from the pots and inserted them in a desiccator. The desiccator with the gaskets and nickel ampules was moved into dry box with inert nitrogen atmosphere.

When the humidity in the dry box (shown in Fig 3) was under 5 ppm we put the weighted in ampules with flange connection. We then placed the tested gaskets in the flange connections and sealed individual connections.

**Fig. 3. Dry box (Placed in Research Centre Rez)**

For the initial experiments we have available 5 types of sealing and 8 ampules with flange connection so we will test selected sealing twice. We moved the sealed ampules from desiccator in a furnace, that does not have regulated atmosphere, and the surfaces of the ampules are surrounded by air. The long-term initial test will run for 3 months at the temperature of 873 K. If the ampule is properly sealed than at the temperature 873 K the pressure of nitrogen above the melt of LiF-BeF2 will be absolute 300 kPa. This test is comparable to the tests carried out by authors Sridharan, Allen [7].

### D. *Thermogravimetric analysis (TGA)*

When choosing suitable candidates for flexible part of the gasket comparative analysis of temperature resistance are made for simultaneously usable materials that can be applied for sealing nodes of fluoride melts.

At fig. 4 is a summary of thermogravimetric analysis in the oxidation atmosphere (21 % O2 and 79 % N2) for following materials: A – mica foil, B – graphite foil reinforced by stainless sheet (316L) for high temperatures and presses, C – Graphite foil reinforced by stainless sheet (316L) for high presses, D – Graphite foil not reinforced by stainless sheet, E – Loose expanded graphite (non-pressed).

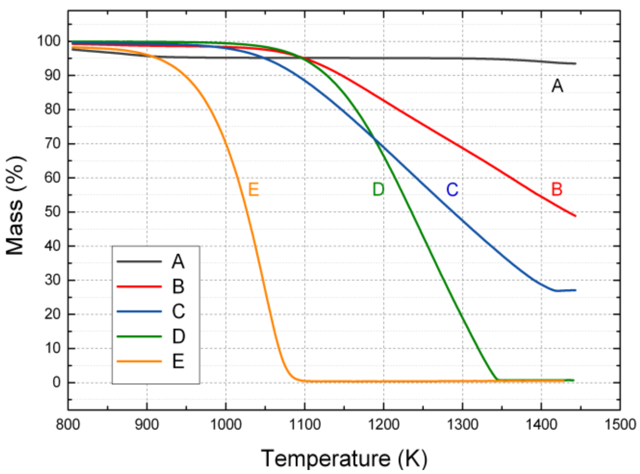


**Fig. 4. TGA analysis material**

Material A represents mica that starts sealing due to its thermal expansion at temperatures about 373 K. That leads to greater tightening force applied at the connection. But it has a very good thermal stability in oxidant atmosphere up to 1500 K. In contrary, the graphite sealing, that is using compressed expanded graphite with 95–99 % purity, resists temperature up to 1000 K. For comparison was used analysis of pure expanded graphite before compression that start to degrade quickly at temperatures about 900 K.

At fig. 5 is an example of diferencial thermogravimetric analysis (DTA) in the oxidation atmosphere for a mica material.

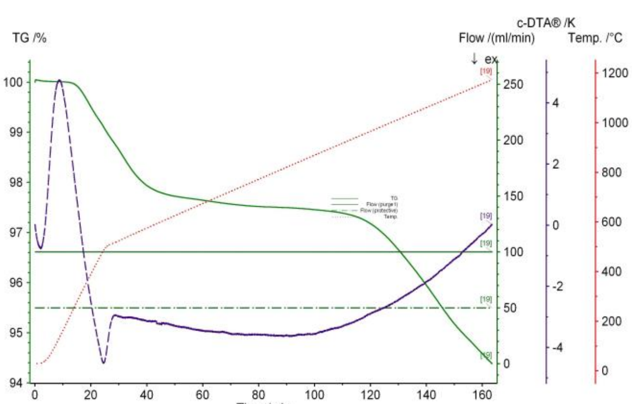


**Fig. 5. DTA analysis material**

The methods to increase the thermal resistance of graphite are based mostly in doping the expanded graphite by exposing it to boric acid. Impregnation of small amount of $B_2O_3$ (2- 4 %) increases the thermal stability of graphite foil in air (it increases the onset oxidation temperature by ~150 K) and also improves the mechanical properties [3], [4]. For commercial use is necessary to subject all suitable materials to long-term testing of thermal stability under operating pressure and evaluate them as composite gasket.

## V. CONCLUSION

For selection and optimization of the suitable materials applicable in the environment of melted fluoride salts were specified individual procedures for long-term testing of individual components and the whole gasket junction as well.

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