DOI 10.52209/1609-1825_2021_3_72 UDC 620.193.4

Corrosion Study of Materials for Electrolyzer Used for Pyrochemical Reprocessing of Spent Nuclear Fuel Based on Cold Crucible Technique

[1]**KARELIN Vladimir,** *Dr. Tech. Sci., Professor, vakarelin@tpu.ru,*
[1]***YUDAKOVA Arina,** *student, group 0482, asy15@tpu.ru,*
[1]**MIKLASHEVICH Dmitriy,** *student, group 0481, dmm8@tpu.ru,*
[1]*Tomsk Polytechnic University, Russia, 634050, Tomsk, Lenin Avenue, 30,*
**corresponding author.*

Abstract. *The application of a cold crucible technique to a pyrochemical electrolyzer used in the method of oxide electrodeposition, which is a method of pyrochemical processing of spent oxide nuclear fuel, is proposed as a means of increasing corrosion resistance. The electrolyzer is subjected to severe corrosion, consisting of molten salt and aggressive gas. In this study, corrosion tests of some metals were carried out in a 2CsCl – NaCl melt at temperature 923 K with purging with chlorine gas under controlled temperature conditions of the material. The results showed that the corrosion rate of some materials was significantly reduced due to the cooling effect of the material. In particular, the Hastelloy C-22 alloy demonstrated excellent corrosion resistance with a corrosion rate of just under 0.01 mm / year in both the molten salt and vapor phases due to the control of the material surface at temperature 473 K. Finally, an engineering-scale crucible consisting of Hastelloy C-22 alloy was manufactured to demonstrate the main function of a cold crucible. The cold crucible induction melting system and the new hastelloy crucible concept have shown good compatibility in terms of heating and cooling.*

Keywords: *corrosion, cold crucible technique, reprocessing of spent nuclear fuel, Hastelloy C-22.*

Introduction

The method of electrochemical production of oxides has been researched all over the world as a method of pyrochemical processing of spent oxide nuclear fuel based on molten salt, and it is expected that a compact facility can be built by integrating with fuel production using vibration compaction methods [1]. Initially, this method was developed by the Research Institute of Nuclear Reactors (NIIAR) in Russia [2-4]. Two methods for extracting plutonium from spent nuclear fuel have been proposed as methods for the electric release of oxide, namely, the deposition of simple plutonium dioxide (PuO_2) and the electrodeposition of mixed uranium and plutonium oxides (MOX-fuel) [5]. All operations are performed in the main element of the electrolyzer during pyrochemical processing – a crucible. The service life of the crucible material in terms of corrosion damage is considered a significant problem for the method of electric oxide release due to the harsh corrosive environment, including corrosive gases and high temperatures. Pyrographite was used as a crucible material for an electrolyzer in the NIIAR. This material has good electrical conductivity and mechanical strength, but carbon suffers seriously in an oxygen atmosphere with high temperatures necessary for the deposition of plutonium oxide and the electrodeposition of MOX-fuel. Accordingly, the possibility of using a new corrosion protection technology should be studied in order to extend the service life of the crucible.

The corrosion resistance of ceramics under pyrochemical conditions was studied [6, 7]. Ceramics can be a promising material for use in conditions of exposure to aggressive gases at high temperatures. However, ceramics have never been used as a structural material for technological equipment used for processing spent nuclear fuel in processes such as fuel dissolution, moreover, the welding characteristics of ceramics and its resistance to loads are not as good as those of metals. Thus, the use of metal containers is necessary to ensure the reliability of the installation. The cold crucible method is considered a promising method for processing structural materials in environments of moderate corrosion.

In this study, corrosion tests of several metals in a 2CsCl – NaCl melt were carried out with purging with chlorine gas while controlling the temperature of the material using air cooling. Promising materials have been proposed that have shown good corrosion resistance under pyrochemical conditions.

Brief description of the pyrochemical processing method

The scheme of the method of electrolytic production of oxides based on MOX deposition is shown in Figure 1 [8]. In this method, most of the fuel components are dissolved in molten 2CsCl-NaCl by purging with chlorine gas at 923 K. The uranium in the fuel is dissolved as the uranyl ion UO_2^{2+}, and the plutonium is dissolved as Pu^{4+} in the molten salt through chlorination.

The noble metals (NM) in the fission products (FP) and part of the uranium are isolated from the dissolved particles by prior electrolysis after the fuel is dissolved. The noble metals are precipitated with uranium dioxide on a pyrographite cathode. The need to separate UO_2 from electrodeposition may appear in order to improve the uranium recovery coefficient. Then, the electrodeposition of MOX is performed in a salt melt, which is blown with oxygen, chlorine and argon gases. At this stage, Pu^{4+} is transited to PuO_2^{2+} by purging with O_2 and Cl_2 gases, and then PuO_2 is reduced as MOX at the cathode by electrolysis with UO_2. Finally, the minor actinides are separated as precipitation by adding sodium carbonate and sodium phosphate.

All these processes are carried out in a crucible-type electrolyzer at high temperatures. Therefore, the electrolyzer suffers from aggressive environment, including corrosive gases such as chlorine and oxygen, at high temperatures.

The design of the apparatus for conducting corrosion tests

The corrosion testing apparatus was designed in such a way that they could be carried out in a salt melt with purging with chlorine gas, during the control of the temperature of the material.

The scheme of the device for corrosion testing is shown in Figure 2. The apparatus mainly consisted of an electric oven, a quartz cell and a cooler for samples. The cooling device was of the rod type and consisted of a Hastelloy alloy. Hastelloy alloys have excellent resistance to pitting, corrosion cracking and oxidizing atmosphere.

The test samples and thermocouples attached to the cooling device are schematically shown in Figure 3. The ring-shaped test samples were put on the outside of the cooler and cooled from the inside by supplying air to the device.

In order to make possible a thorough study of the corrosive behavior of the crucible material, the samples were contacted with both the vapor phase and the molten salt phase.

Table shows the conditions under which the tests were carried out and shows the materials that were subjected to corrosion resistance tests as part of the study.

The following hastelloy alloys were selected as test samples: stainless steel (310S, 304L), carbon steel (SS400), zirconium, titanium, tantalum, copper and graphite. The purity of samples made of materials such as zirconium, titanium, tantalum, copper and graphite exceeded 99.5%. Three types of alloys such as Hastelloy (Hastelloy C-22 (C-22), Hastelloy G-30 (G-30) and Hastelloy X (X)) were used in corrosion tests.

Results of researches

Figure 4 shows data about the corrosion rate of several materials. The temperature of the surface of these materials in the melted salt was maintained at the level of 473 K, and the surface temperature of the samples in the vapor always was kept at the level of 393 K.

In the figure 4, the corrosion rates are the average value for the two samples. All Hastelloy alloys have good resistance to corrosion; particularly, the corrosion rate of Hastelloy grade C-22 was slightly less than 0.01 mm/year, both in the salt melt and in the vapor phase.

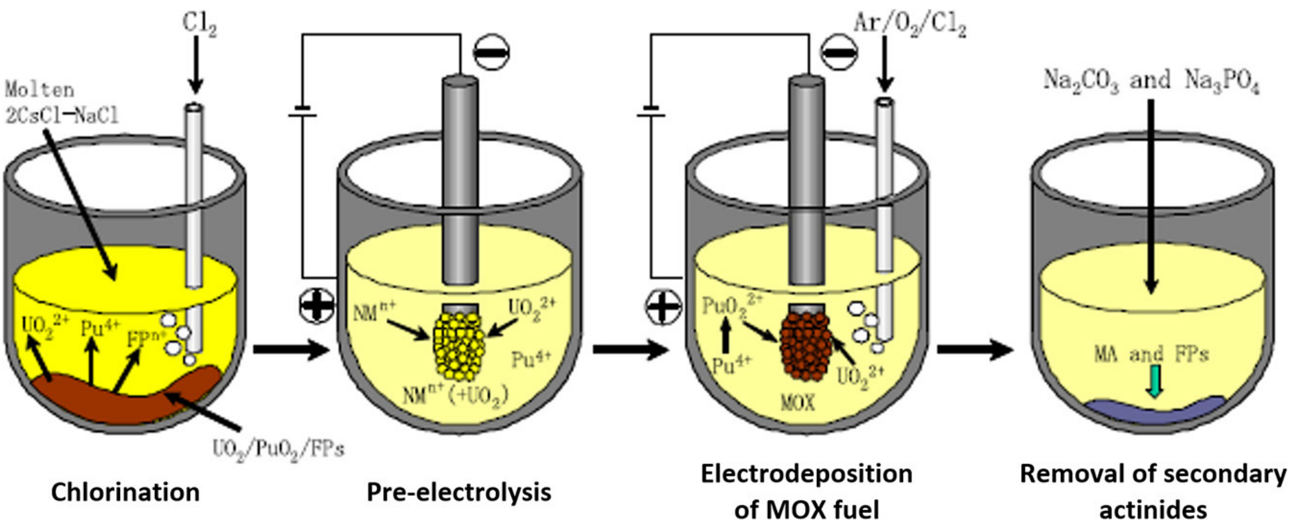

Figure 1 – The process of electrodeposition of oxides based on the deposition of MOX fuel

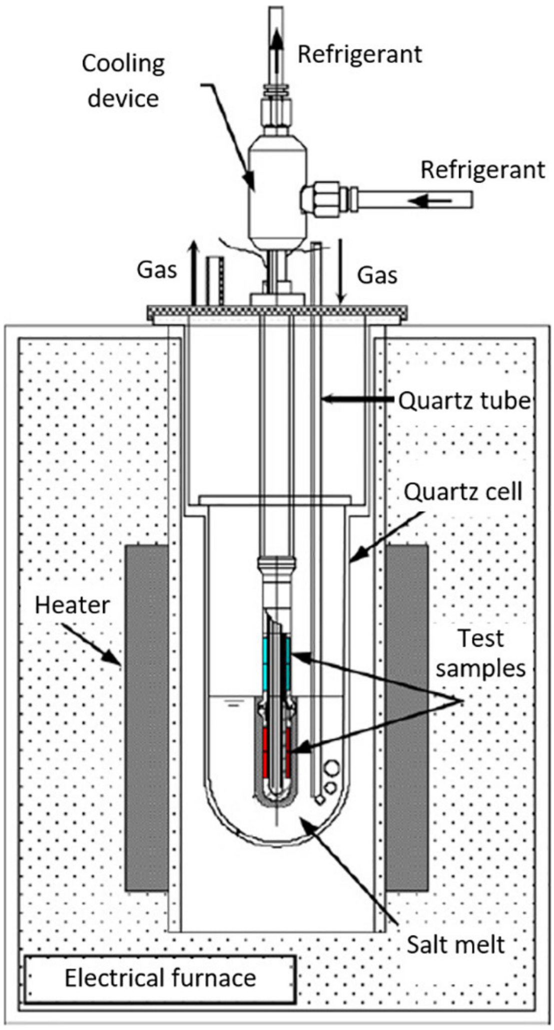

Figure 2 – The diagram of the device for conducting corrosion tests

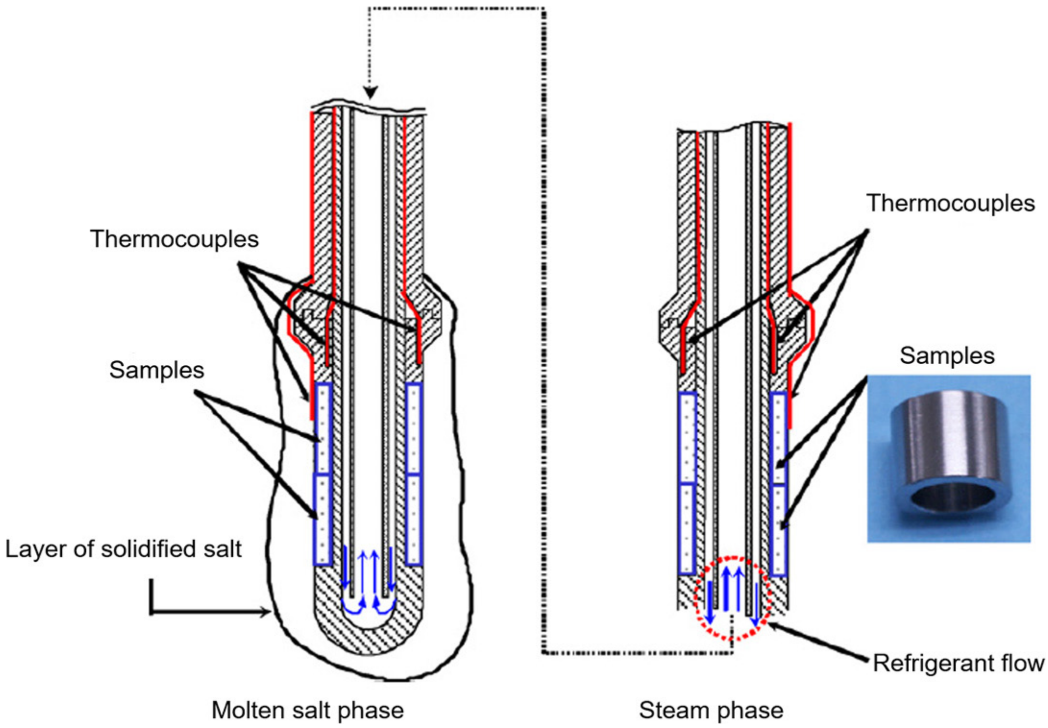

Figure 3 – The arrangement of samples and thermocouples on the cooling device

Test conditions	
Materials	Hastelloy alloys C-22, G-30, X; SS400, Zr, Ti, Ta, Cu, C (Graphite)
Type of salt	2CsCl-NaCl
Flow rate Cl_2	150 ml / min
Melt temperature	923 K
Minimum temperature of the samples in the salt melt	473 K
Sample cooling method	Air
Location of samples in a cell	Melt phase and steam phase
Test time	6 hours

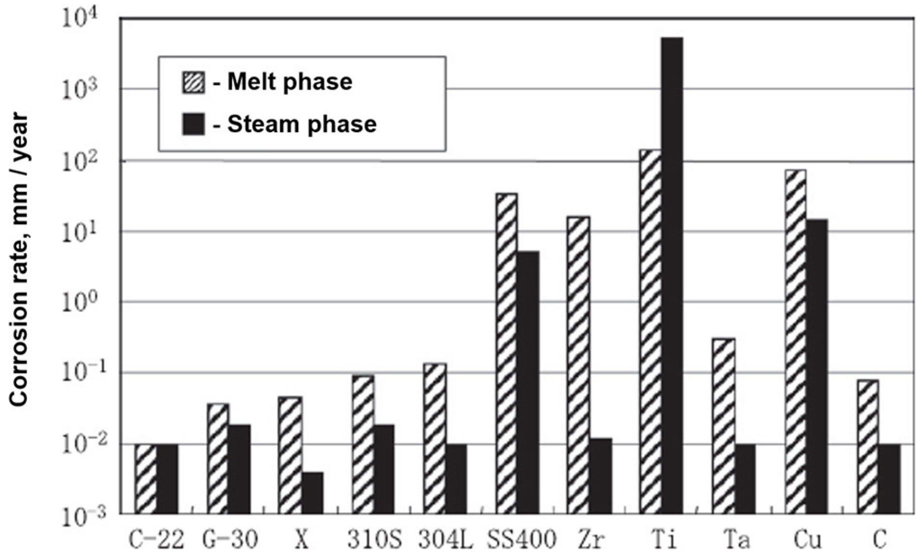

Figure 4 – Corrosion rate of materials

The effect of the cold crucible on the corrosion rate was significant. In a salt melt, the corrosion rate at a material temperature of 573 K corresponds to approximately 1/1000 of the corrosion rate at 923 K. In the temperature range of the formation of a solidified salt layer, which is below the melting point of 2CsCl–NaCl, the corrosion rate in the molten salt was lower than in the vapor phase. On the other hand, the corrosion rate was higher in the region above the melting point in the molten salt phase than in the vapor phase. This variable behavior of the corrosion rate in both molten salt and vapor phases suggests that the melting point acts as a border due to the barrier effect of the solidified salt.

The solidified salt layer plays an important role as a corrosion inhibitor of the crucible material, since it protects the surface of the material from the effects of molten salts and aggressive gas. It is admitted to be one of the advantages of the cold crucible method, which makes it possible to obtain a pyrochemical electrolyzer with good corrosion resistance. Therefore, it was experimentally shown that the cold crucible method provides a significant improvement in corrosion resistance. Figure 5 shows the dependence of the corrosion rate on the surface temperature.

According to the results of corrosion tests, Hastelloy C-22 was signed as the most proper material for an improved pyrochemical electrolyzer.

Conclusions

Corrosion resistance tests of a variety of materials for use in an electrolyzer with a cold crucible for reprocessing spent nuclear fuel have been carried out. It is proved that the Hastelloy S-22 alloy has the greatest resistance to the effects of an aggressive environment.

It was experimentally shown that the cooling effect of the crucible significantly increases the corrosion resistance. In particular, the Hastelloy C-22 alloy showed excellent corrosion resistance both in the melted salt and in the vapor phase. Therefore, it was shown that the use of an improved pyrochemical electrolyzer based on the cold crucible method has a significant advantage in the form of significantly improved corrosion resistance.

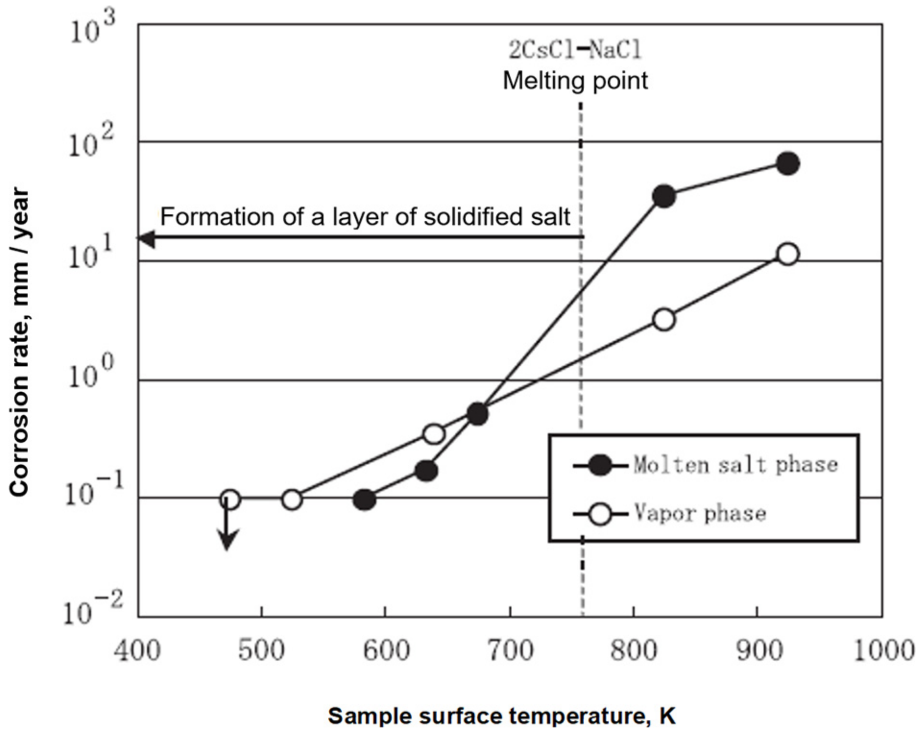

Figure 5 – Dependence of corrosion of Hastelloy C-22 alloy samples on temperature

REFERENCES

1. K. Fujii, A. Inoue, T. Namba, K. Sato, in: Proceedings of Global'97, Yokohama, Japan, 1997, p. 756.
2. O.V. Skiba, Y.P. Savochkin, A.V. Bychkov, P.T. Porodnov, L.G. Babikov, S.K. Vavilov, in: Proceedings of Global'93, Seattle, USA, 1993, p. 1344.
3. A.V. Bychkov, S.K. Vavilov, P.T. Porodnov, O.V. Skiba, in: Proceedings of Global'93, Seattle, USA, 1993, p. 1351.
4. A.V. Bychkov, S.K. Vavilov, P.T. Porodnov, A.K. Pravdin, G.P. Popkov, K. Suzuki, Y. Shoji, T. Kobayashi, in: Proceedings of Global'97, Yokohama, Japan, 1997, p. 912.
5. T. Kobayashi, S.K. Vavilov, F. Sato, M. Myochin, T. Namba, K. Fujii, J. Nucl. Sci. Technol. 42 (2005) 295-300.
6. M. Aso, S. Tamura, T. Namba, in: Proceedings of Global'99, Wyoming, USA, 1999, p. 659.
7. M. Takeuchi, T. Kato, T. Koizumi, Corrosion Eng. 52 (2003) 403-417.
8. S. Ninagawa, M. Nagao, Technol. Rev. 23 (2000) 19-22.

Пайдаланылған ядролық отынды пирохимиялық өңдеуге арналған электролизер материалының тоттануға төзімділігін суық тигель технологиясын қолдана отырып зерттеу

[1]***КАРЕЛИН Владимир Александрович,*** *т.ғ.д., профессор, vakarelin@tpu.ru,*

[1]****ЮДАКОВА Арина Сергеевна,*** *студент, 0482 топ, asy15@tpu.ru,*

[1]***МИКЛАШЕВИЧ Дмитрий Михайлович,*** *студент, 0481 топ, dmm8@tpu.ru,*

[1]*Томск политехникалық университеті, Ресей, 634050, Томск, Ленин даңғылы, 30,*

**автор-корреспондент.*

Аңдатпа. *Пайдаланылған оксидті ядролық отынды пирохимиялық өңдеу әдісі болып табылатын оксидті электрмен тұндыру әдісінде қолданылатын пирохимиялық электролизерге суық тигель әдісін қолдану коррозияға төзімділікті арттыру құралы ретінде ұсынылады. Электролизер балқытылған тұз бен агрессивті газдан тұратын қатты коррозияға ұшырайды. Бұл зерттеу 2CsCl – NaCl балқымасындағы кейбір металдардың коррозиялық сынақтарын 923 К кезінде материалдың бақыланатын температуралық жағдайында хлор газын үрлеу арқылы жүргізді. Нәтижелер кейбір материалдардың коррозия жылдамдығы материалды салқындату әсерінен айтарлықтай төмендегенін көрсетті. Атап айтқанда, Хастеллой С-22 қорытпасы балқытылған тұзда да, бу фазаларында да коррозия жылдамдығы жылына 0,01 мм-ден сәл аз болатын тамаша коррозияға төзімділікті көрсетті, 473 К-де материалдың бетін бақылау арқылы. Соңында, Хастеллой С-22 қорытпасынан тұратын инженерлік масштабтағы тигель суық тигельдің негізгі функциясын көрсету үшін жасалды. Суық тигельмен индукциялық балқыту жүйесі және жаңа хастеллой тигель тұжырымдамасы қыздыру және салқындату тұрғысынан жақсы үйлесімділікті көрсетті.*

Кілт сөздер: *коррозия, суық тигель әдісі, пайдаланылған ядролық отынды өңдеу, Хастеллой С-22.*

Исследование коррозионной стойкости материала электролизера для пирохимической переработки отработавшего ядерного топлива с применением технологии холодного тигля

[1]***КАРЕЛИН Владимир Александрович,*** *д.т.н., профессор, vakarelin@tpu.ru,*
[1]****ЮДАКОВА Арина Сергеевна,*** *студент, группа 0482, asy15@tpu.ru,*
[1]***МИКЛАШЕВИЧ Дмитрий Михайлович,*** *студент, группа 0481, dmm8@tpu.ru,*
[1]*Томский политехнический университет, Россия, 634050, Томск, пр. Ленина, 30,*

**автор-корреспондент.*

Аннотация. *Применение метода холодного тигля к пирохимическому электролизеру, используемому в методе оксидного электроосаждения, который представляет собой метод пирохимической переработки отработавшего оксидного ядерного топлива, предлагается в качестве средства повышения коррозионной стойкости. Электролизер подвергается сильной коррозии, состоящей из расплавленной соли и агрессивного газа. В данном исследовании были проведены коррозионные испытания некоторых металлов в расплаве 2CsCl – NaCl при 923 К с продувкой газообразным хлором в контролируемых температурных условиях материала. Результаты показали, что скорость коррозии некоторых материалов была значительно снижена из-за эффекта охлаждения материала. В частности, сплав Хастеллой С-22 продемонстрировал отличную коррозионную стойкость со скоростью коррозии чуть менее 0,01 мм / год как в расплавленной солевой, так и в паровой фазах за счет контроля поверхности материала при 473 К. Наконец, тигель инженерного масштаба, состоящий из сплава Хастеллой С-22, был изготовлен для демонстрации основной функции холодного тигля. Система индукционной плавки с холодным тиглем и новой концепцией тигля из хастеллоя показала хорошую совместимость с точки зрения нагрева и охлаждения.*

Ключевые слова: *коррозия, метод холодного тигля, переработка отработавшего ядерного топлива, Хастеллой С-22.*

REFERENCES

1. K. Fujii, A. Inoue, T. Namba, K. Sato, in: Proceedings of Global'97, Yokohama, Japan, 1997, p. 756.
2. O.V. Skiba, Y.P. Savochkin, A.V. Bychkov, P.T. Porodnov, L.G. Babikov, S.K. Vavilov, in: Proceedings of Global'93, Seattle, USA, 1993, p. 1344.
3. A.V. Bychkov, S.K. Vavilov, P.T. Porodnov, O.V. Skiba, in: Proceedings of Global'93, Seattle, USA, 1993, p. 1351.
4. A.V. Bychkov, S.K. Vavilov, P.T. Porodnov, A.K. Pravdin, G.P. Popkov, K. Suzuki, Y. Shoji, T. Kobayashi, in: Proceedings of Global'97, Yokohama, Japan, 1997, p. 912.
5. T. Kobayashi, S.K. Vavilov, F. Sato, M. Myochin, T. Namba, K. Fujii, J. Nucl. Sci. Technol. 42 (2005) 295-300.
6. M. Aso, S. Tamura, T. Namba, in: Proceedings of Global'99, Wyoming, USA, 1999, p. 659.
7. M. Takeuchi, T. Kato, T. Koizumi, Corrosion Eng. 52 (2003) 403-417.
8. S. Ninagawa, M. Nagao, Technol. Rev. 23 (2000) 19-22.