**Determination of the metallic and oxide compounds in model fuel based on metallic uranium containing uranium dioxide, metallic neodymium, cerium as well as neodymium and cerium oxides**

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**Abstract**

The paper is devoted to the determination of the oxygen concentration in the model mixtures with different content of U, Nd, Ce and their oxides as well as metallic Pd. The “bromine method” and reductive melting were used. The combination of these methods allowed evaluating the ratio of metallic and oxide phases of uranium and rare-earth metals in the studied samples.

1. INTRODUCTION

Development of the methods allowing the determination of the degree of "metallization" of the oxide mixtures of rare-earth metals (REM) and uranium is one of the major criteria for their successful electrochemical reduction during the lithium electrochemical cathode extraction at the electrolysis of the molten mixture of lithium chloride and lithium oxide. There is a safe “bromine method” engineered for determination of the uranium metallic phase in the presence of its oxide. This method is based on the selective dissolution of the metallic uranium from its mixture with oxide in the bromine ethyl acetate solution (Br2-EtOAc) [1,2]. The interaction between bromine and metallic uranium results in the formation of bromides, whereas uranium dioxide does not interact with bromine. Therefore, uranium bromides enter a liquid medium of the ethyl acetate solution and the concentration of uranium oxide (II) in the solid deposit is determined by the IСPAES method. However, despite wide usage of this method in different research [3,4], it can’t be recognized as the best one for the study of the rea-earth metals and their oxides. Reductive melting of oxides in a graphite crucible allows one to determine reliably the concentration of bonded oxygen in the sample using auxiliary molten metals. The combination of the common chemical analysis for the desired elements and two above mentioned methods provides an algorithm, which allows determining the ratio between the metallic and oxide phases of different metals in the studied samples. In this particular case: “bromine technique” provide a reliable data on the relation of metallic uranium and uranium dioxide, i.e. oxygen bonded to uranium. At the same time the method of reductive melting determines the total oxygen concentration in the analyzed sample, which, considering the amount of oxygen bonded to uranium, allows calculating the quantity of oxygen bonded to REM atoms.

The algorithm presented in this work combines common chemical analysis of the samples, “bromine method” and reductive melting. Such combination allows determining the ratio of the metallic and oxide phases of desired metals in the studied samples.

1. EXPERIMENTAL

**2.1. Preparation of samples**

To prepare model mixtures, we used metallic uranium of the TU 95 2054-2003 grade of the 95.5 wt. % purity and oxygen concentration of 0.0094 wt.% according to the reductive melting; UO2, Nd2O3 and CeO2 powders with the main component concentration not less than 99.99 wt.%. The oxygen concentration in these powders was analytically calculated. Metallic palladium of the 99.99 wt.% purity was added into some mixtures

The REM oxide powders were preliminary dried on the hot plate at the temperature of 200°С for 2 h and then were put into a glove box with argon atmosphere, oxygen concentration not exceeding 10 ppm and moisture concentration under 0.1 ppm. The powders were annealed in a furnace in a glove box at 700°С for 2 h.

**2.2. Gas hot extraction method**

The method of reductive melting involves the evolution of the sample oxygen into a gas phase in the form of carbon monoxide, its further catalytic transformation into carbon dioxide and measuring its quantity with gas analysis methods [6,7].

The gas evolves under the influence of high temperature and reagents under conditions, when the gaseous products are continuously removed from the reaction area. To decrease the partial pressure of the evolved gases to the negligibly small quantity the reaction cell is either pumped by a vacuum pump (vacuum-melting) or washed with the flow of pure inert gas or gaseous reagent (melting in a carrier-gas flow).

Carbon is used as a reducing agent; the samples are melted in the carbon crucible. Therefore, oxygen transfers to the gas phase as carbon monoxide. The successful analysis requires an almost complete evolution of the gas from the sample during a short period of time and transfer of the evolved gas to the gas analyzer. In addition, the process conditions should minimize the device gas evolution (blank correction), as they influence the device sensitivity and analysis accuracy. Obviously, the blank correction becomes smaller, when the gases evolve faster. There are two main factors that determine the rates of the reductive melting processes and the degree of the admixtures extraction to the gas phase: temperature and a preliminary degassed metallic melt in the crucible or metal with low gases concentration, which is melted with the sample.

The parameters of the reductive melting of the samples were verified by the thermogravimetric analysis of the possible reactions of the REM oxides reduction in the graphite crucible by the HSC-9 program. The calculation results allowed us to assume that the Nd2O3 and CeO2 reduction by carbon should be performed at the temperatures of 2000°C and above. Metallic uranium is one of the components of the analyzed sample. Obviously, it will interact with the graphite crucible, in addition this reaction will be more intense than in the cases of Nd2O3 and CeO2. To provide a smoother reaction, uranium alloying metal, which is inert to carbon, may be introduced into the system. Nickel is one of such metals [8]. On the one hand nickel may decrease significantly the uranium activity [8], on the other hand under the discussed temperatures nickel dissolves carbon and transports it to the uranium oxide sample.

1. RESULTS AND DISCUSSION

The optimal parameters of the reductive melting of the U-UO2 mixtures were experimentally verified before analysis according to the suggested algorithm. It was found that to obtain reproducible analysis results the uranium mixtures’ melting should be performed at the temperature of 2200°С in nickel tubes, because nickel melts and dissolves well carbon and uranium. Thus, the uranium dioxide reduction reaction proceeds in a liquid phase, which increases both the process rate and the process completeness.

The results of oxygen determination in the model samples are provided in Tables 1-8. The “metallization” degree **β**(theory) in the model mixture was determined as a ratio of the uranium weight in the metallic phase to the sum of uranium weights (mU) in metallic and oxide phases (mU + mUO2). Three compositions of model mixtures with uranium dioxide concentrations of 2, 5 and 10 wt.% were studied. When calculating **β**(exp) the sample solutions’ volumes were not considered, as all volumes were equal.

Table 1 provides the results of the “metallization” degree of the model mixtures using the “bromine method” and Table 2 presents the results obtained by the reductive melting.

TABLE 1. “Metallization” degree of the model U-UO2 mixtures determined using the “bromine method”

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| UO2,wt.%  in the mixture | mU,  mg | mUO2,  mg | [U]U,  mg/l | [U]UO2,  mg/l | β(theory) | Averageβ  (theory) | β(exp.) | Averageβ  (exp.) | Discrepancy, % |
| 10 | 118 | 12.06 | 2363 | 216 | 91.73 | 91.78 | 91.62 | 91.65 | 0.14 |
| 114 | 11.49 | 2249 | 204 | 91.83 | 91.68 |
| 5 | 136 | 6.53 | 2743 | 122 | 95.94 | 95.62 | 95.93 | 95.58 | 0.04 |
| 137 | 7.4 | 2812 | 131 | 95.45 | 95.54 |
| 128 | 6.87 | 2351 | 112 | 95.47 | 95.45 |
| 2 | 157 | 3.16 | 2581 | 56.19 | 98.25 | 98.26 | 97.80 | 97.83 |  |
| 157 | 3.18 | 2879 | 54 | 98.24 | 97.78 | 0.44 |
| 157 | 3.07 | 3096 | 55 | 98.30 | 97.91 |  |

TABLE 2. “Metallization” degree of the model U-UO2mixtures using determined the reductive melting method

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| [UO2], wt.%  in the mixture | mU,  mg | mUO2,  mg | [O],  wt.%, theory | β(theory) | | Averageβ(theory) | [O],  wt.%,  theory | β(exp.) | | Averageβ  (exp.) | Discrepancy,% |
| 10 | 131 | 13.2 | 1.11 | | 91.84 | 91.81 | 1.13 | | 91.39 | 91.31 | 0.51 |
| 133 | 13.4 | 1.11 | | 91.84 | 1.22 | | 90.64 |
| 130 | 13.1 | 1.11 | | 91.84 | 1.25 | | 90.40 |
| 106 | 10.7 | 1.12 | | 91.83 | 1.03 | | 92.25 |
| 124 | 12.7 | 1.13 | | 91.71 | 1.08 | | 91.87 |
| 5 | 128 | 6.7 | 0.61 | | 95.59 | 95.53 | 0.58 | | 95.71 | 95.41 | 0.12 |
| 129 | 7.1 | 0.64 | | 95.37 | 0.60 | | 95.55 |
| 140 | 6.4 | 0.54 | | 96.13 | 0.58 | | 95.60 |
| 98 | 5.8 | 0.68 | | 95.03 | 0.71 | | 94.58 |
| 2 | 158 | 3.7 | 0.29 | | 97.89 | 98.14 | 0.29 | | 97.80 | 97.99 | 0.15 |
| 145 | 3.1 | 0.26 | | 98.07 | 0.29 | | 97.78 |
| 158 | 3.3 | 0.26 | | 98.16 | 0.27 | | 97.91 |
| 152 | 3.0 | 0.24 | | 98.21 | 0.24 | | 98.21 |
| 142 | 2.8 | 0.24 | | 98.21 | 0.24 | | 98.22 |
| 126 | 2.5 | 0.24 | | 98.19 | 0.28 | | 97.86 |
| 140 | 2.8 | 0.25 | | 98.21 | 0.26 | | 98.04 |
| 142 | 2.8 | 0.24 | | 98.29 | 0.25 | | 98.09 |

Tables 1 and 2 illustrate that in both cases oxygen determination in the initial metallic phase changes the value of the “metallization” degree only in two decimal places, which is a satisfactory difference. In addition, the obtained experimental values of the “metallization” degree agree well with the theoretical values and the values of the “metallization” degree, obtained by two different methods, differ not more than by 0.3%.

The results of the experimental determination of oxygen concentration by the reductives melting method in the mixtures of metallic uranium and REM oxides are provided in Tables 3-8. The theoretical concentration of oxygen in the samples, which was calculated according to the stoichiometric concentration in the (Nd2O3 – 14.26 wt.% and CeO2 – 18.59 wt.%) oxides and oxide weights in the sample. The values of oxygen concentration in the ([O] in Nd2O3) oxide sample solely may be analyzed as determination of the oxygen concentration in the case, when the uranium sample is considered as the melt for creation of a liquid metallic bath. Thus, we may calculate a relative standard deviation (RSD). The comparison of the theoretically and experimentally obtained values of oxygen concentration in the samples illustrates a high accuracy of the reductive melting method for oxygen concentration determination. The average difference in the values reported in Tables 3-8 does not exceed 6.2%.

TABLE 3. Analysis of the oxygen concentration in the U-9wt%Nd2O3 mixture

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| № | m(U), mg | m(Nd2O3), mg | [O] in Nd2O3,  wt.% | [Nd2O3]  weighted sample,  wt.% | [O] in weighted sample,  wt.% | | Discrepanсy,  % |
| exp. | theory |
| 1 | 114 | 11.7 | 13.44 | 9.31 | 1.250 | 1.327 | 5.80 |
| 2 | 116 | 11.5 | 14.61 | 9.00 | 1.317 | 1.286 | -2.41 |
| 3 | 98 | 9.8 | 14.53 | 9.09 | 1.320 | 1.296 | -1.85 |
| 4 | 119 | 11.7 | 13.72 | 8.95 | 1.228 | 1.277 | 3.84 |
| 5 | 110 | 11 | 13.48 | 9.09 | 1.225 | 1.296 | 5.48 |
| 6 | 86 | 8.4 | 14.09 | 8.90 | 1.253 | 1.269 | 1.26 |
| 7 | 66 | 6.6 | 13.41 | 9.09 | 1.219 | 1.296 | 5.94 |
| 8 | 65 | 6.5 | 14.17 | 9.09 | 1.288 | 1.296 | 0.62 |
| 9 | 75 | 7.8 | 15.53 | 9.42 | 1.462 | 1.343 | -8.86 |
| Average concentration, wt.%  Theoterical concentration, wt.% | | | 14.11  14.26 |  | 1.285 | 1.299 | 1.08 |
| RSD, % | | | 5 |  |  |  |  |

TABLE 4. Analysis of the oxygen concentration in theU-2wt%Nd2O3 mixture

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| № | m(U), mg | m(Nd2O3), mg | [O] в Nd2O3,  wt.% | [Nd2O3]  weighted sample,  wt.% | [O] in weighted sample,  wt.% | | Discrepanсy,  % | |
| exp. | theory |
| 1 | 167 | 3.4 | 13.86 | 1.99 | 0.276 | 0.284 | | 2.82 |
| 2 | 184 | 3.7 | 13.59 | 1.97 | 0.268 | 0.281 | | 4.63 |
| 3 | 164 | 3.3 | 13.69 | 1.97 | 0.270 | 0.281 | | 3.91 |
| 4 | 150 | 2.9 | 14.75 | 1.90 | 0.280 | 0.270 | | -3.70 |
| 5 | 142 | 2.8 | 14.51 | 1.93 | 0.280 | 0.276 | | -1.45 |
| 6 | 170 | 3.4 | 13.26 | 1.96 | 0.260 | 0.280 | | 7.14 |
| 7 | 187 | 3.8 | 13.87 | 1.99 | 0.276 | 0.284 | | 2.82 |
| 8 | 188 | 3.8 | 13.48 | 1.98 | 0.267 | 0.282 | | 5.32 |
| 9 | 180 | 3.7 | 14.40 | 2.01 | 0.290 | 0.287 | | -1.05 |
| 10 | 137 | 2.9 | 14.39 | 2.07 | 0.298 | 0.296 | | -0.68 |
| Average concentration, wt.%  Theoterical concentration, wt.% | | | 13.92  14.26 |  | 0.277 | 0.282 | | 1.77 |
| RSD, % | | | 4 |  |  |  | |  |

TABLE 5. Analysis of the oxygen concentration in the U-9wt%CeO2 mixture

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| № | m(U), mg | | m(CeO2), mg | | [O] inCeO2,  wt.% | [CeO2]  weighted sample,  wt.% | [O] in the weighted sample,  wt.% | | Discrepancy,  % |
| exp. | Theory |
| 1 | | 120 | | 11.9 | 16.17 | 9.02 | 1.460 | 1.677 | 12.94 |
| 2 | | 105 | | 10.4 | 17.41 | 9.01 | 1.569 | 1.675 | 6.33 |
| 3 | | 120 | | 11.8 | 18.66 | 8.95 | 1.671 | 1.664 | -0.42 |
| 4 | | 112 | | 11.2 | 17.46 | 9.09 | 1.587 | 1.690 | 6.09 |
| 5 | | 108 | | 10.8 | 16.28 | 9.09 | 1.480 | 1.690 | 12.43 |
| 6 | | 101 | | 10.3 | 17.86 | 9.25 | 1.653 | 1.720 | 3.90 |
| 7 | | 134 | | 13.5 | 17.04 | 9.15 | 1.559 | 1.701 | 8.35 |
| 8 | | 115 | | 11.4 | 16.80 | 9.02 | 1.515 | 1.676 | 9.61 |
| 9 | | 132 | | 13.3 | 18.99 | 9.15 | 1.738 | 1.701 | -2.18 |
| 10 | | 128 | | 12.9 | 17.64 | 9.16 | 1.615 | 1.701 | 5.06 |
| Average concentration, wt.%  Theoterical concentration, wt.% | | | | | 17.43  18.59 |  | 1.585 | 1.690 | 6.21 |
| RSD, % | | | | | 5 |  |  |  |  |

TABLE 6. Analysis of the oxygen concentration in the U-2wt%CeO2 mixture

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| № | m(U), mg | m(CeO2), mg | [O] inCeO2,  wt.% | [CeO2]  weighted sample,  wt.% | [O] in weighted sample,  wt.% | | Discrepancy,  % |
| exp. | theory |
| 1 | 134 | 2.6 | 18.63 | 1.90 | 0.354 | 0.353 | -0.28 |
| 2 | 125 | 2.4 | 17.44 | 1.88 | 0.328 | 0.350 | 6.29 |
| 3 | 132 | 2.8 | 17.41 | 2.08 | 0.361 | 0.386 | 6.48 |
| 4 | 152 | 3.1 | 16.51 | 1.99 | 0.323 | 0.371 | 12.94 |
| 5 | 135 | 2.7 | 17.44 | 1.96 | 0.342 | 0.364 | 6.04 |
| 6 | 169 | 3.3 | 18.78 | 1.92 | 0.360 | 0.356 | -1.12 |
| 7 | 147 | 3 | 17.86 | 2.00 | 0.357 | 0.372 | 4.03 |
| 8 | 129 | 2.7 | 16.89 | 2.05 | 0.346 | 0.381 | 9.19 |
| 9 | 177 | 3.6 | 17.47 | 1.99 | 0.348 | 0.370 | 5.95 |
| 10 | 179 | 3.5 | 17.35 | 1.92 | 0.333 | 0.356 | 6.46 |
| 11 | 187 | 3.7 | 18.05 | 1.94 | 0.350 | 0.361 | 3.05 |
| Average concentration, wt.%  Theoterical concentration, wt.% | | | 17.62  18.59 |  | 0.346 | 0.365 | 5.21 |
| RSD, % | | | 4 |  |  |  |  |

TABLE 7. Analysis of the oxygen concentration in the U-3.75wt%Nd2O3-3.75wt%CeO2-7.5wt%Pd mixture

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| № | m(U), mg | m(Nd2O3), mg | m(CeO2), mg | m(Pd), mg | [O] in weighted sample,  wt.% | | Discrepancy,  % |
| exp. | theory |
| 1 | 54 | 2.36 | 2.36 | 4.72 | 1.26 | 1.413 | -10.82 |
| 2 | 69 | 3.00 | 3.00 | 6.01 | 1.21 | 1.409 | -14.11 |
| 3 | 34 | 1.47 | 1.47 | 2.95 | 1.49 | 1.403 | 6.17 |
| 4 | 27 | 1.19 | 1.19 | 2.38 | 1.36 | 1.423 | -4.41 |
| 5 | 28 | 1.20 | 1.20 | 2.41 | 1.54 | 1.393 | 10.53 |
| 6 | 24 | 1.04 | 1.04 | 2.08 | 1.48 | 1.402 | 5.60 |
| 7 | 27 | 1.17 | 1.17 | 2.33 | 1.53 | 1.399 | 9.36 |
| Average concentration, wt.% | | | | | 1.41 | 1.406 | 0.29 |
| RSD,% | | | | | 0.134 |  |  |

TABLE 8. Analysis of the oxygen concentration in the U-5wt%Nd2O3-5wt%CeO2-5wt%Pd mixture

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| № | m(U), mg | m(Nd2O3),  mg | | m(CeO2),  mg | m(Pd),  mg | [O] in weighted sample,  wt.% | | Discrepancy,  % |
| exp. | theory |
| 1 | 70.98 | | 4.18 | 4.18 | 4.18 | 1.78 | 1.74 | -2.39 |
| 2 | 74.12 | | 4.36 | 4.36 | 4.36 | 1.59 | 1.74 | 8.54 |
| 3 | 73.27 | | 4.31 | 4.31 | 4.31 | 1.83 | 1.74 | -5.26 |
| 4 | 80.92 | | 4.76 | 4.76 | 4.76 | 1.67 | 1.74 | 3.94 |
| 5 | 75.06 | | 4.42 | 4.42 | 4.42 | 1.68 | 1.74 | 3.36 |
| 6 | 79.99 | | 4.71 | 4.71 | 4.71 | 1.83 | 1.74 | -5.26 |
| 7 | 74.12 | | 4.36 | 4.36 | 4.36 | 1.78 | 1.74 | -2.39 |
| 8 | 66.56 | | 3.92 | 3.92 | 3.92 | 1.69 | 1.74 | 2.79 |
| Average concentration, wt.% | | | | |  | 1.73 | 1.74 | 0.42 |
| RSD,% | | | | | | 0.086 |  |  |

The measurement results illustrate that such combined approach provides reproducible results on the determination of the oxygen concentration in the model samples containing U, UO2, REM oxides and metallic Pd, which agree well with theoretical data, calculated using known quantities of components in the model sample.

1. CONCLUSION

The bromine method makes it possible to separate the metallic and oxide forms of uranium, and thus to determine the amount of oxygen released from the corresponding oxide. The reductive melting method, while using the correct analysis conditions, makes it possible to determine the total oxygen content in the sample given by all components of the model system. Both methods are complementary and both allow one to estimate the oxygen concentration both in the entire model mixture system and in individual components. When the bromine method and the reductive melting method are used together, reproducible results are obtained for determining the oxygen concentration in model samples containing U, UO2, REM oxides, and metallic Pd. The results are in good agreement with the theoretical data calculated from the known amounts of components in the model sample.

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