Fabrication of nano-micro-sized $^{14}$C enriched constructive elements in plasma deactivation treatment of irradiated reactor graphite

A S Petrovskaya$^1$, A Yu Kladkov$^2$, S V Surov$^2$, M R Stakhiv$^3$, A B Tsyganov$^4$

$^1$ Plasma application department, Spectrum-Micro LLC, St.Petersburg, Russia
$^2$ Science and Innovation JSC, Moscow, Russia
$^3$ Rosenergoatom JSC, Moscow, Russia

anita3425@yandex.ru

Abstract. We propose a new fabrication method for the meta-material said "beta-active nano-sandwich" (for example, enriched with radioisotope $^{14}$C, etc.) by a plasma sputtering technology that we are developing for the decontamination of nuclear power plants constructions. This new kind of beta-active nano-materials can be a valuable product resulting from nuclear deactivation process and be useful for nuclear medicine applications and creation of advanced beta-voltaic batteries. Plasma sputtering device operation is based on a “dry” plasma decontamination method – the ion sputtering of radionuclides from the radioactively polluted surface (e.g., irradiated reactor graphite). We present calculations results of the plasma sputtering device operating parameters: anode and cathode surface temperature, discharge input power density, equivalent current density, ion sputtering and mass-transfer rates of nano-layers from the processed graphite surface.

1. Introduction

A new method of metananomaterial creation can be deduced from the technology that we are developing for the surface deactivation of the nuclear power plants irradiated constructions.

It important be noted that one of the current nuclear industry problems is the irradiated reactor graphite deactivation during decommissioning of the nuclear power plants, as well as findings of effective method for decontaminating of the nuclear power equipment internal surfaces sedimented with radionuclides from the water of reactor primary circuit during operation [1].

Currently, there is a number of costly and environmentally unfriendly technologies for the decontamination of the surface of nuclear equipment contaminated with radionuclides during operation and repair. First of all, these technologies include the various chemical etching methods, which lead to large volumes of liquid radioactive waste. Additionally, before the nuclear industry there is an actual problem of the decontamination and utilization of irradiated reactor graphite due to the coming period of the graphite reactors intensive decommissioning around the world. The following technologies are considered as applicable candidates: plasma combustion technologies with crushing into fine fractions [2], chemical or thermal treatment (e.g., [3]). However, ones lead to the formation of secondary radioactive tails of large volume. Important sub-task in this way is removal of the $^{14}$C isotope (half-lifetime of 5730 years) from irradiated graphite, these radionuclides have been formed...
during operation in significant quantities. Experimental studies of the spatial localization of the $^{14}$C isotope inside of the irradiated graphite bulk [4] showed that considerable amounts of the $^{14}$C isotope may be concentrated at or in close vicinity under the bulk surface. The technology we are developing transfers sputtered radionuclides from the isotope $^{14}$C enriched irradiated graphite surface to a multi-layer structure formed on the anode substrate – "beta-active nano-sandwich". So, our technology delivers not only the deactivation treatment of reactor graphite, but also a new useful product [5].

2. Method

Graphite bulk surface is used as a cathode. Flat tantalum collector plate, used as anode, of 1 mm thick covered with 10 mm ceramics heat insulator is placed at 1 mm above the flat surface of the graphite bulk (thickness 600 mm). Argon flow is provided between cathode and anode gap and direct current plasma discharge is ignited at the pressure of $P \sim 0.1$-1 bar. The operating voltage on the discharge gap is applied by the power supply source in the range of 400-600 V, the discharge current density is regulated in the range (0.01 – 1) A/cm$^2$. The gap between the collector and the graphite surface may be variable depending on the argon pressure, but it have to be near to 100 electron mean free paths at the working gas concentration. Sputtered by plasma discharge atoms (and radioactive isotopes) from the cathode surface are diffusing in argon gas and are condensing on the collector. The collector plate and the gas pumping line that provides argon removal from the discharge zone are cooled by external circulating coolant to a temperature sufficient for the condensation of the sputtered atoms of active isotope on the collector surface. Note that the flowing argon is not bound chemically with any sputtered atoms, so it is free from radioactivity and can be re-circulating again. After the treated surface (the cathode) is atomized to a predetermined depth, the electrode is positioned to a new location on the surface of graphite bulk and the process is repeated until the total deactivation of the contaminated surface is completed [6].

This technology makes it possible to transfer the radioactive isotopes enriched layer from the treated surface to the collector (anode), so various radionuclides ($^{14}$C, $^{60}$Co, $^{134}$Cs, $^{137}$Cs, etc) can be selectively condensed on the collector. So, the solid multi-layer structure consisting of the preferred type of radioactive atoms condensed on the collector in layer-by-layer manner (from nano to microsize scale) may be formed in dependence of the collector temperature. Then the collector plate with the concentrated high radioactivity sediment is periodically extracted for a compact dumping, or for the useful application in the nuclear medicine as a high enriched concentrate of the desired isotope (in particular, $^{14}$C), or for the creating of a new type of a beta-voltaic batteries. Thus, this technology can be applied for the creation a new kind of metanamomaterials - "beta active nano-sandwich" with radioactive isotopes enriched nano-micro-sized layers formed by the controlled ion sputtering.

Figure 1 shows the general view of the plasma source device (section view): the discharge is ignited between the graphite surface - the grounded cathode (K) and the positively charged cooled collector – the anode (A). The inert gas is fed into the discharge gap between (A) and (K) in the direction 1. The fast electrons 2 generated in the discharge collide with the inert gas atoms 3 and provide the positively charged inert gas ions 4. The ions 4 acquire kinetic energy in the cathode sheath electric field of the discharge and knock out atoms 5 from the cathode (K) material. The voltage $V$ distribution curve along the discharge gap is shown on Figure 1 at the right side.

Figure 2 schematically illustrates (not to scale) the plasma sputtering device: the treated graphite bulk as the cathode (e.g., RBMK reactor type with thickness $d = 600$ mm) (1), the argon-filled discharge gap (thickness $p = 1$ mm) (2), the collector consisting of two elements: the flat tantalum plate $L1 = 1$ mm thick (3), covered with ceramics heat insulator (4) thick of $L2 = 10$ mm.

3. Results. Calculation of the temperature regimes of the plasma sputtering device

Temperatures on the anode A and cathode K surfaces are the most important operating parameters of the plasma sputtering device, since the temperature control allows selective separation and condensation on the collector surface of various radioactive atoms sputtered from the cathode surface under treatment. For example, according to the data on the saturated vapor pressure of various
elements [7], the density of saturated calcium vapor is $10^4$ Torr at the collector temperature of 650 K. In this way it can be presumed that the isotope $^{41}$Ca will be effectively deposited on the collector, while others, more volatile radioactive atoms (e.g., $^{134}$Cs, $^{137}$Cs) will remain in the gaseous phase and will condense downstream inside of the pumping line at the lower surface temperature. To form the $^{14}$C enriched nano-sandwich it is necessary to rise the temperature of collector plate up to 1800 K to prevent the condensation of other more volatile species, so some heat shield at the outer surface of the collector have to be mounted.

For the plasma sputtering device (figure 2) we have calculated the temperature distribution in four media: graphite cathode (1), argon plasma (2), collector (3,4) in the stationary approach. The heat transfer equations system was solved for four contacting media 1,2,3,4 (figure 2) with the heat flux continuity requirements and the temperatures boundary conditions 300K at $x = -d$, $x = L2$. Based on the distribution of the electric potential in the discharge gap (figure 1, right side) we assume that the entire energy input to the discharge is released near the surface of the cathode, so the heat source can be defined as the delta function at the boundary $x = 0$. It is assumed that the external boundary surfaces of said anode $x = L2$ and the cathode $x = -d$ being cooled and maintained at 300K.

The cathode surface temperature $T_K$ depends on the discharge input power density and may reach up to 2000K. So, we took into account the radiation transfer ($\sigma T^4$, $\sigma$- Stefan–Boltzmann constant) between the cathode and the collector. For the plasma sputtering device the cathode $T_K$ and anode $T_A$ surface temperature depending on the discharge input power density and equivalent current density at 600V discharge voltage were calculated for two types of the anode thermal insulation: the ceramic based on SiC and SiO$_2$, see table 1 and table 2, respectively.

The sputtering rate of the cathode material $V_P$, was estimated by the formula:

$$V_P = \frac{K \cdot j \cdot M_c \cdot e \cdot N_A \cdot \rho}{h}$$

where $V_P = h / t$ is the sputtering rate (nm/s), $K$ - sputtering coefficient of cathode material by argon ions, $M_c$ - is the mass of atoms of the material (carbon) (g/mol), $e$ - is the electron charge (C), $\rho$ - is the density of the material (g/cm$^3$), $N_A$ - is the Avogadro number (mol$^{-1}$), $j$ - is the ion current density (A/cm$^2$). Graphite sputtering coefficient by argon ions $K$ is 0.1 at the energy 600 eV [8].

The estimates based on the Richardson–Dushman equation [9] showed that the thermo-electrons current density from the cathode surface can be neglected under described conditions.
Table 1.

| $T_i$ (K) | $T_A$ (K) | $Q$ (W/m$^2$) | $I$ (A/cm$^2$) | $V_p$ (nm/s) |
|-----------|-----------|---------------|---------------|--------------|
| 600       | 301       | 1.44E5        | 0.024         | 1.8          |
| 800       | 305       | 2.11E5        | 0.035         | 2.6          |
| 1000      | 312       | 2.96E5        | 0.050         | 3.7          |
| 1400      | 350       | 5.46E5        | 0.090         | 6.7          |
| 1700      | 412       | 8.57E5        | 0.140         | 10           |
| 2000      | 552       | 1.24E6        | 0.200         | 15           |

Table 2.

| $T_i$ (K) | $T_A$ (K) | $Q$ (W/m$^2$) | $I$ (A/cm$^2$) | $V_p$ (nm/s) |
|-----------|-----------|---------------|---------------|--------------|
| 600       | 361       | 1.34E5        | 0.022         | 1.6          |
| 800       | 452       | 2.07E5        | 0.035         | 2.6          |
| 1000      | 581       | 2.91E5        | 0.048         | 3.6          |
| 1400      | 937       | 5.33E5        | 0.088         | 6.6          |
| 1700      | 1279      | 8.25E5        | 0.137         | 10           |
| 2000      | 1676      | 1.16E6        | 0.194         | 14           |

4. Conclusions

In this paper we presented new plasma method for the meta-material "beta-active nano-sandwich" formation based on the ion sputtering of the nano- and micro-sized radioactive contaminated surfaces. The "beta-active nano-sandwich" may have useful application in the nuclear medicine and for the creation of advanced beta-voltaic batteries. Important operating parameters of the plasma sputtering device were calculated.

Acknowledgment

The reported study was funded by RFBR according to the research project № 18-32-00679 mol_a.

References

[1] Fachinger J, Podruhzina T and von Lensa W 2008 Nuclear Engineering and Design 11 3086
[2] Bespala E V, Pavlyuk A O, Izmost’ev A M, Kotlyarevskiy S G and Mikhalets A M 2016 RF Patent Specification 2580818
[3] Theodosiou A, Jones A N, Burton D, Powell M, Rogers M and Livesey V B 2018 Journal of Nuclear Materials 507 208
[4] LaBrier D and Dunzik-Gougar M L 2014 Journal of Nuclear Materials 448 113
[5] Petrovskaya A S, Kladkov A Yu, Surov S V and Tsyganov A B 2018 Problems of atomic science and technology Series: Nuclear and Reactor Constants 4 185
[6] Petrovskaya A S, Tsyganov A B, Kladkov A Yu, Surov S V, Stakhiv M R and Polischuk V A 2018 Foc. Int. Conf. on Electrical Engineering and Photonics (Saint-Petersburg) (Piscataway, New Jersey: Institute of Electrical and Electronics Engineers -IEEE ) p 230
[7] Honig R E and Kramer D A 1969 RCA Rev. 30 285
[8] Anderson H H and Bay H L 1981 Sputtering Yield Measurements Topics in Applied Physics. Sputtering by Particle bombardment I. Physical Sputtering of Single-Element Solids ed R Berisch (Berlin-Heidelberg-New York: Springer-Verlag) chapter 4 pp 145-218
[9] Raiser Yu P 1992 Gas Discharge Physics (Moscow: Publishing House Science) p 536