Diffuse vacuum arc with cerium oxide hot cathode

R Kh Amirov, N A Vorona, A V Gavrikov, G D Liziakin, V P Polistchouch, I S Samoylov, V P Smirnov, R A Usmanov, I M Yartsev and A S Ivanov

Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
E-mail: ravus46@yandex.ru

Abstract. Diffuse vacuum arc with hot cathode is one of the perspective plasma sources for the development of spent nuclear fuel plasma reprocessing technology. Experimental data is known for such type of discharges on metal cathodes. In this work discharge with cerium dioxide hot cathode was studied. Cerium dioxide properties are similar to uranium dioxide. Its feature as dielectric is that it becomes conductive in oxygen-free atmosphere. Vacuum arc was studied at following parameters: cathode temperatures were between 2.0 and 2.2 kK, discharge currents was between 30 and 65 A and voltages was in range from 15 to 25 V. Power flows from plasma to cathode were estimated in achieved regimes. Analysis of generated plasma component composition was made by radiation spectrum diagnostics. These results were compared with calculations of equilibrium gaseous phase above solid sample of cerium dioxide in close to experimental conditions. Cerium dioxide vacuum evaporation rate and evaporation rate in arc were measured.

1. Introduction
Plasma separation technology is a perspective method of spent nuclear fuel (SNF) reprocessing along with existent radiochemical and developing gaseous fluoride and pyroelectrophysical methods [1]. One of the problems must be solved during this technology creation is a conversion of condensed SNF substance in a plasma state. Vacuum arc with evaporating hot cathode is one of the promising high productivity plasma sources for this purpose. Feature of this discharge is a relatively low cathode current density (about 10 A/cm²) and micro particles of cathode erosion products are absent in arc plasma, that is not typical for contracted arcs. Study of diffuse vacuum arc on hot gadolinium cathode modeling uranium have shown possibility of realizing vacuum arc regime producing singly ionized plasma jet with high ionization degree [2]. This mode is a necessary condition for achieving high efficiency of SNF plasma reprocessing method [1]. However the main component of the most widespread nowadays SNF is uranium dioxide and further study of this discharge as a plasma source should be done on oxide cathode.

2. Cerium oxide as an arc operating substance
Election of simulating substance—analogue of uranium dioxide based on comparison of physical properties of oxides and the constituent metals. Such physical properties as electron configuration of metals, correlation between oxides and corresponding metals melting temperatures, saturation vapor pressures, enthalpies of sublimation and oxides work functions were analyzed.
Electron configuration of cerium ([Xe] 4f° 5d° 6s°) is similar to uranium ([Rn] 5f° 6d° 7s°). They have completed last s electron orbital but f and d orbitals are incomplete. Melting temperatures of respective oxide-metal pairs are close and also have the same difference (UO₂/U—3.1/1.3 kK; CeO₂/Ce—2.9/1.1 kK) [3,4]. Correlation between uranium and uranium dioxide saturation vapor pressures is such that uranium dioxide evaporates slower at the same temperature. Similar correlation is typical for cerium oxide. Calculated uranium and cerium dioxide saturation vapor pressures is such that uranium dioxide evaporates slower at the same temperatures of respective oxide-metal pairs are close and also have the same difference at temperature $T_c$ 

One of the values determining properties of vacuum arcs is a ratio of evaporating atoms flux to flux of thermionic emission at certain cathode temperature. These ratios for uranium and cerium dioxides at temperature of 2 kK are much less than unit: $\xi(UO_2) = 10^{-4}$, $\xi(CeO_2) = 10^{-2}$ [5,7]. So, it is expected that properties of vacuum arcs with uranium dioxide and cerium dioxide cathodes will be similar.

Note that at standard conditions for temperature and pressure cerium dioxide has a low electrical conductivity because its band gap $\Delta$ equals 3.41 eV [4]. Uranium dioxide is a semiconductor at this conditions ($\Delta = 1.3$ eV) [4].

### 3. Experiment

#### 3.1. Experimental technique

The discharge was initiated in a vacuum chamber at the residual gas pressure less than 10 mPa. Rectifier with output voltage of 380 V was used as arc power source. Investigated substance was placed in molybdenum crucible with outer diameter of 25 mm and height of 14 mm. Diameter of crucible outlet was 14 mm. Electron-beam heater (EBH) with power up to 1.5 kW was situated under the crucible that allowed changing its temperature at fixed arc current. Typical crucible operating temperature was in range of 2.0–2.2 kK. The water-cooled steel disk with centered hole of 15 mm in diameter was used as an arc anode. The distance between electrodes was about 30 mm.

The crucible temperature $T_c$ was measured by brightness-temperature pyrometer. By estimations the difference between measured temperature and mean temperature of cathode surface due to temperature drop in crucible wall was less than 3%. Plasma radiation was registered by spectrometer SDH-IV within wavelength range of 200–900 nm.

Initial cerium oxide was a pale yellow powder that was sintered in molybdenum crucible before the experiment at temperatures of 1.9–1.95 kK during about 10 minutes. After sintering oxide became similar to a black tablet with the diameter of 14 mm and height of 4 mm. Its mass was about 3 g. Energy dispersive X-ray analysis of sintered cathode showed that it still was an oxide material.

In accordance with [8] during CeO₂ heating in oxygen free atmosphere it dioxides to CeO₂ where $x = 1.95–1.90$ due to loss of oxygen atoms and transition of some ions from Ce⁴⁺ to Ce⁴⁺ state. Such transition causes a sharp increase of electrical conductivity at temperatures higher than 0.5 kK. Additional experiments carried out by us have verified described properties. In oxygen atmosphere non-stoichiometric cerium oxide oxidizes again and electrical conductivity returns to initial values. In this way at the cathode operating regime ($T_c \geq 2$ kK) cerium oxide was in conductive state. This cerium oxide property means that adjustment of plasma SNF reprocessing technology should be done with the help of vacuum arc just with hot cathode.

Experiments were carried out by the following scheme. The crucible with sintered oxide was heated by EBH up to the temperature of 1.9 kK, after that voltage was applied to the interelectrode gap ($\approx 380$ V) and heating process was continued. Breakdown was registered at temperature $T_c \approx 2.05$ kK. Saturation vapor pressure at this temperature is about 5 Pa [5]
that corresponds to the vapor density of $2 \times 10^{14}$ cm$^{-3}$. After arc initiation pressure in vacuum chamber increased from 10 to 20 mPa and after 10–30 seconds it returned to initial values.

Figure 1 presents the photo of diffuse vacuum arc. Vacuum arc with currents in range of 30–65 A was obtained at values of EBH power $N = 700–1000$ W. At maximum current values depending on cathode temperature (or EBH power) discharge voltage was changing in rage of 15–25 V. The discharge is characterized by absence of irregular voltage oscillations and absence of micro particles of cathode erosion products, which signs were observed neither on experiment video recordings nor on surrounding surfaces of the discharge (anode, thermal shields).

Periodically on the anode surface a contraction of the arc was observed. Apparently it appeared because of a low electrical conductivity of cerium oxide film settling on cooling anode. After local film heating in the anode spot the diffuse discharge on the anode surface was restored.

3.2. Power fluxes to the cathode
Similar to the method described in [9] heat flux $Q$ incoming to the cathode from discharge was measured. For this purpose a calibration of the crucible temperature was done. In other words power of EBH required for crucible heating to different temperatures was measured. Matching EBH power in arc regime and form calibration curve providing the same cathode temperature allow us to determine $Q$. Value $Q$ is a difference between heat flux incoming from plasma to the cathode $Q_p$ and heat loss caused by thermionic emission $Q_{em}$.

Heat mode of the oxide cathode generally is similar to heat mode of gadolinium cathode describing in [9]. At the arc current $I = 65$ A regime when arc heats cathode was realized, i.e. heat flux $Q_p$ exceeded heat loss $Q_{em}$. At EBH power $N = 700–750$ W heat flux $Q$ was changing in range of 80–120 W and arc voltage was about 15 V.

3.3. Cathode evaporation rate
By weighting method average cathode evaporation rate was measured at arc current of 65 A. Average cathode operating time was about 10 minutes. Also it was done for cerium oxide evaporation without arc ($I = 0$). These results are shown on the figure 2.
Figure 2. Oxide evaporation rate versus return crucible temperature.

Figure 2 is also presents calculated evaporation rate in effusion approximation based on saturation vapor pressure data from [5]. For calculation we used crucible outlet area of 1.54 cm² and assumed Clausing’s coefficient of 0.85 [10].

We should note that, because of 3% temperature drop in crucible wall, its temperature measured without arc (I = 0) could be higher than cathode temperature. It corresponds to the blue line calculated implying temperature error of 3%. On the other hand evaporation rate in arc regimes (I = 65 A) was achieved when arc heated the cathode (see previous section) and measured crucible temperature could be lower than cathode temperature. The green line on the figure 2 illustrates this possible uncertainty in temperature value. In general measured evaporation rate data correlates with calculations based on available saturation vapor pressure data of cerium oxide.

3.4. About plasma composition
Plasma reprocessing technology implies operating with plasma flow of different element of SNF therefore component composition of plasma from source should be known for further monitoring of separation process. For the qualitative knowledge of plasma composition generating in vacuum arc with cerium oxide cathode registration of its radiation spectra was done. Spectrum analysis showed presence of atomic and ion radiation lines of cerium, molybdenum and oxygen: Ce I, Ce II, Ce III, Mo I, Mo II, O I, O II [11]. Radiation lines of CeO molecules was not observed [12].

Indirect information about arc plasma composition (base components without quantitative characteristics) could be estimated from calculation of equilibrium gaseous phase composition above cerium oxide sample. Calculation of gaseous phase composition was carried out with the help of processing package IVTANTHERMO [13] in close to experimental conditions: cathode temperature $T_c = 2.1$ K, external pressure $P = 1.33 \times 10^{-2}$ Pa (it was assigned by presence of 0.0001 mole of argon). Condensed phase was a mixture of 1 mole of CeO₂ and 0.1 mole of Mo—crucible material. In result of calculation a molar volume of gaseous phase and molar quantity of substances presented there were obtained (table 1).

According to the presented data the main component of gaseous phase is a molecules of cerium monoxide. Its dissociation energy (CeO = Ce + O) equals 8.1 eV [4]. Energies are necessary
Table 1. Calculated cerium oxide gaseous phase composition.

| Substance | Quantity, mol |
|-----------|--------------|
| Ar        | 0.0001       |
| CeO       | 1.0×10^0     |
| O         | 7.5×10^-1    |
| MoO₂      | 7.3×10^-2    |
| O₂        | 2.1×10^-2    |
| MoO₃      | 1.7×10^-2    |
| MoO       | 8.9×10^-3    |
| Mo        | 9.9×10^-4    |
| Ce        | 4.2×10^-7    |
| Mo₂       | 3.6×10^-10   |

for the first and the second ionization of cerium atoms are 5.5 and 10.8 eV correspondingly [3]. Matching both values and taking into account presence of Ce III radiation lines in plasma spectrum we can expect a considerable dissociation of monoxide molecules.

4. Conclusion
As a conclusion let us list the main obtained results. In the paper the firstly obtained diffuse vacuum arc with evaporating cerium oxide cathode modeling uranium dioxide was described. It was noted that at standard conditions for temperature and pressure cerium dioxide demonstrates dielectric properties and in arc condition it operates as a conductor. Experimental data on heat flux incoming from discharge to the cathode was obtained and its value was in range of 80–120 W. Cathode evaporation rate was in range of 1.5–3.5 mg/s. Measured evaporation rate data correlates with calculations based on available saturation vapor pressure data of cerium oxide. On qualitative level plasma composition of vacuum arc was estimated taking into account spectroscopic measurements and calculation of equilibrium gaseous phase above condensed sample of cerium dioxide in close to experimental conditions. Radiation atomic and ion lines of cerium, molybdenum and oxygen was observed in plasma spectrum. Assumption of high dissociation degree of cerium monoxide in arc plasma was made.

Note also that there are three circumstances showing absence of cathode current contraction in the described discharge. Low value of cerium oxide work function (\( \phi = 2.75 \) eV [7]) allow cathode to provide almost all arc current density at operating temperature due to thermionic emission, thus likely there are no conditions for appearance of current contraction. As shown in the paper, cathode evaporation rate in arc conditions is close to thermal evaporation rate that also indicates absence of cathode spots. Discharge voltage measurements also showed absence of irregular voltage oscillations that is not typical for contracted arcs.

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