**Redox behavior of ruthenium in nuclear glass melt: ruthenium dioxide reduction reaction**

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**Abstract**

Among platinoid fission products, ruthenium is a key element during the vitrification of high-level waste because it is poorly soluble in the glass matrix. It occurs mainly as RuO2 particles and sometimes as Ru0 particles in the glass melt and final cooled glass. Because the physical properties of ruthenium are very different from those of glass, the RuO2 particles change the glass melt properties such as the rheology, thermal conductivity and electrical conductivity. In addition, because the Ru0 properties are even more distinct from the glass properties, glass melts can be more sensitive to the presence of Ru0 particles. Thus, ruthenium speciation, specifically the RuO2 reduction into Ru0, was investigated in air and glass environments, and the experimental results were compared to thermodynamic calculations (Calphad method).

Under air conditions, the thermodynamic modeling and experimental results are in good agreement. They show a reduction of RuO2 at 1403 °C and 1405 ± 7 °C, respectively. The experimental results indicate that the Ru0 particle formation may result from an autocatalysis mechanism, which involves the gaseous species of ruthenium.

In the investigated glass, the first Ru0 particles appear at approximately 1280 °C. At 1280 °C < T < 1400 °C, only few particles are observed attributed to minor reduction phenomena: local redox reaction with iron or disproportionation reaction. At higher temperatures (T > 1400 °C), a much more significant reduction takes place. This one is attributed to the decomposition under temperature and oxygen pressure conditions, predicted by thermodynamic calculations. Based on the results obtained under air conditions, it is assumed that the reduction mechanism involves dissolved ruthenium species.

**Keywords**

Redox, nuclear glass, thermodynamic modeling, ruthenium

1. Introduction

Ruthenium is a fission product resulting from fission reactions of uranium or plutonium. In spent UO2 or mixed oxide (MOX) fuels, ruthenium occurs in a Pd–Rh–Ru–Mo–Tc metallic alloy called the “epsilon phase” or “white phase” [1].

In France, PUREX spent-fuel reprocessing is performed in nitric acid to separate uranium and plutonium, which can be recycled, from the other fission products and minor actinides. During this step, less than half the ruthenium amount is solubilized in the acid solution [2-4]. The other part remains solid, mainly as oxidized RuO2 precipitates [2]. During the subsequent calcination step of the high-level waste, both forms of ruthenium are introduced into the calciner, and ruthenium complexes transform into ruthenium oxide or more complex oxides like Na3RuO4 [5]. The obtained powder is then poured into the furnace and melted in an alumino-borosilicate glass at approximately 1150 °C [6].

Unlike the other fission products, ruthenium (as well as Pd–Te alloys) is poorly soluble in many glass matrixes [7-14]. Its solubility depends on the glass melt composition and temperature: it increases with the basicity and temperature. In typical glass compositions, the Ru-solubility ranges between a few weight ppm [14, 15] to 80 weight ppm [7].

Because of this low solubility and the ruthenium concentration, which ranges from 1 to 2 wt%, ruthenium occurs in glass mostly in the form of undissolved RuO2 particles. These particles are micrometric polyhedrons or needles, depending on the reaction pathway during calcination [5]. Furthermore, they tend to agglomerate together and/or with Pd–Te beads [16-18]. Figure 1 presents scanning electron microscopy (SEM) images of simulated nuclear glass. The micrographs show clearly the distribution and shape of RuO2 particles, which are associated with Pd–Te beads.

Figure 1: SEM images of typical simulated nuclear glass. Grey needles and white round particles are RuO2 particles and Pd–Te beads, respectively.

Because these RuO2 particles are denser and more conductive than the surrounding glass (Table 1), they modify the physical properties of the glass. Under specific conditions, metallic ruthenium Ru0 can be observed. Because Ru0 is even denser and more conductive than RuO2, the glass properties can be further modified. Therefore, predicting and controlling the redox of ruthenium and managing the homogeneous distribution of these conductive particles are crucial for ensuring optimal elaboration conditions.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Properties | Ru0(s) | RuO2 | Glass | Glass with 8 wt% RuO2 |
| Density (25 °C) | 12.3 | 6.97 | 2.5 | / |
| Electrical conductivity (S·m‑1) at 27 °C | 14.4×106  [19] | 2.8×106  [20] | < 10‑8  [21, 22] | ≈ 10‑2 extrapolated from [22] |
| Electrical conductivity (S·m‑1) at 1100 °C | 2.5×106  [19] | ≈ 105 extrapolated from [20] | ≈ 10  [22] | ≈ 30  [22] |

Table 1: Physical properties of glass and ruthenium solid species

Many researchers have experimentally studied the RuO2 reduction reaction in a gaseous atmosphere [23-25]. For instance, Bell and Tagami [23] studied the RuO2 reduction for 10‑2 < p(O2) < 1 atm. They determined that the RuO2 decomposition (RuO2 → Ru0 + O2 + ε(RuO2(g), RuO3(g), RuO4(g))) occurs at 1542 °C at p(O2) = 1 bar and 1403 °C at p(O2) = 0.21 bar. In addition, they measured the equilibrium vapor pressure and calculated the heat of formation and standard entropy of RuO2(s), RuO3(g) and RuO4(g). Jacob *et al.* [25] described the thermodynamic parameters (Gibbs energy, enthalpy and entropy) of the Ru–O system and provided a critical literature review. Later, Brunetti *et al.* [24] measured and modeled the RuO2 dissociation for 10‑4 < p(O2) < 10‑6 bar. All these data are considered in the Calphad assessment developed by Gossé *et al.* [26], which was used for the presented thermodynamic calculations (see § 2.1.).

Furthermore, Okamoto *et al.* [27] and Pinet & Mure [28] studied ruthenium redox in glasses. Okamoto *et al.* applied oxygen partial pressure to the simulated nuclear glass samples, with a controlled atmosphere at p(O2) = 0.21, 2∙10‑3, or 10‑5 bar and in pure Ar. The authors observed that ruthenium dioxide is almost the only ruthenium species in glass at 800 °C at any oxygen pressure. However, at 1400 °C in pure Ar, only metallic ruthenium is stable. At 1000 and 1200 °C, both metallic and dioxide ruthenium forms coexist, even if metallic ruthenium remains predominant. Pinet & Mure measured the oxygen pressure of glass, which contain a mixture of RuO2 and Ru0 at 1000-1200 °C. Their results provide estimates of the oxygen pressure for the RuO2–Ru0 equilibrium. At 1200 °C, the logarithm of the measured oxygen pressure of glass (in bar) is ‑1.85 ± 0.1.

In this study, the RuO2 reduction reaction was studied as a function of the temperature and surrounding environment (air or glass). For the experiments with glass, unlike in Okamoto’s experiments, the p(O2) was determined by the melt itself and not by the atmosphere. The thermodynamic calculations and experimental results were compared, and the mechanisms leading to the formation of Ru0 particles in air and glass melt are proposed in this paper.

1. Materials and methods
   1. Thermodynamic modeling

The thermodynamic calculations presented in this paper were performed with the Calphad method, which determines the thermochemical equilibrium states of a chemical system. This method is based on the minimization of the Gibbs energy functions of phases, which are possibly present in the system. The Gibbs energy G of each phase is defined with respect to the enthalpy of the pure elements at 298.15 K and p = 1 bar in the “stable element reference” (SER) °HSER(298.15 K). Each type of phase is described with its own model [29]:

* Ru0(s) is a pure element; its Gibbs energy is presented in Equation 1:

(1)

where Giφ is the Gibbs energy of the pure element i in the phase φ, °HiSER(298.15 K) is the enthalpy of the pure elements i at 298.15 K and p = 1 bar in the “stable element reference”, T is the temperature, n are integers, and a, b, c and dn, are adjustable parameters for fitting the experimental data.

* RuO2(s) is considered a stoichiometric phase; its Gibbs energy is as follows:

(2)

where GRuO2 is the Gibbs energy of RuO2 (rutile phase) and xi is the atomic fraction of the pure element i in the stoichiometric phase. The other parameters are the same than those described above.

* O(g), O2(g), RuO(g), RuO2(g), RuO3(g), and RuO4(g) are part of the gas phase, which is considered an ideal mixture of species; its Gibbs energy is as follows:

(3)

where Gφ is the Gibbs energy of the gas phase, xi is the atomic fraction of the species i in the gas, Gi is the Gibbs energy of the species i, R is the ideal gas constant, p is the pressure of the gas phase and p0 is the reference pressure set at 1 bar.

All previous mentioned species were considered in the studied Ru–O system, and the development of the databases and optimization of parameters a, b, c and dn were made in [26, 30, 31]. The assessments and calculations presented in this paper were performed with the Thermocalc© package.

Owing to the very poor solubility of platinoids, this thermodynamic modeling approach does not consider the interactions between platinoids and the glass. Their interactions with the surrounding glass was modeled by setting the temperature and oxygen potential; the chemical activity of the ruthenium dissolved in the glass was not considered.

* 1. Sample composition

The ruthenium precursor was a ruthenium dioxide (RuO2) powder from Heraeus (specific surface area of 39.7 m2/g, mean particle diameter of 14 nm, and purity > 99.9%). Two sets of experiments were performed: in air and in glass.

The air samples (samples A) were made from RuO2 powder, which was filled into alumina crucibles.

To prepare the glass samples (samples G), glass frit was grounded into powder and mixed with 5 (samples G5) or 0.5 wt% RuO2 (samples G0.5). Although these RuO2 concentrations are not in the typical range of nuclear glasses, they allow to study morphologies and redox of ruthenium. Indeed, it is assumed that the redox behavior of ruthenium in glass stays the same whatever the RuO2 concentration, provided it is higher than solubility limit and impurity level. For experimental reason (see § 2.3), samples G0.5 are used for oxygen pressure measurements whereas samples G5 are used for heat treatments in order to determine ruthenium speciation and particles morphologies. This high concentration enables to increase the statistic when observing the ruthenium particles by SEM.

The glass frit was industrially pre-elaborated by FERRO at 1350 °C from a simple composition: SiO2 (55 wt%), Na2O (28 wt%), CaO (10 wt%), and Al2O3 (7 wt%). It did not contain multivalent elements, except the Fe2+/Fe3+ couple at impurity level (0.05 wt% Fe2O3).

* 1. Potentiometry measurements

Potentiometry measurements were performed to determine the oxygen partial pressure of the glass with and without ruthenium at high temperatures (approximately 350 g of glass). Potentiometry measurements of the glass with ruthenium are conducted on samples G0.5. Because both 0.5 and 5 wt% RuO2 are higher than the solubility limit of ruthenium in glass and higher than the impurity level of this glass, the p(O2) measurements are assumed to give same results in both cases. To avoid sedimentation and aggregation of ruthenium particles during the measurements, measurements were performed only on the G0.5 sample. A working electrode made of an iridium wire and an Ni/NiO reference electrode were inserted into the glass melt, and the zero-current potential difference was measured [32]. This potential difference is linked to the temperature and oxygen partial pressure of the glass according to Equation 4:

(4)

With ΔE the potential difference, R the ideal gas constant, Tglass the temperature of the glass melt, F the Faraday constant, p(O2)glass the oxygen pressure of the glass and p(O2)ref the reference oxygen pressure linked to the electrode reference. To ensure equilibrium conditions, the glass was heated and treated at the desired temperature for 20 min before starting the measurements. To avoid local concentration effects, the crucible rotated during the measurements.

The logarithm of the oxygen partial pressure of the glass (in bar) at 1200 °C is ‑2.8 ± 0.1. Its oxygen pressure is mainly controlled by the Fe2+/Fe3+ couple, which is the major multivalent impurity of the glass frit.

* 1. Heat treatments in muffle furnace

The heat treatments were performed in a muffle furnace. The samples (approximately 50 mg RuO2 powder for samples A and approximately 10 g of the mixture {glass + 5 wt% RuO2 powder} for the samples G5) were filled into alumina crucibles, which were then introduced into a pre-heated Nabertherm muffle furnace at temperatures between 1200 and 1550 °C for 1 to 4 h. At the end of the experiments, the crucibles were removed from the hot furnace and left to cool in ambient air. For this part of the study, samples G5 are used in order to maximize the ruthenium particles number observed on SEM cross-sections (see § 2.6.).

* 1. Differential thermal analysis/gravimetric thermal analysis

The differential thermal analysis (DTA) and gravimetric thermal analysis (TGA) of the samples A were conducted in a SETARAM SETSYS Evolution apparatus which is not sufficiently sensitive for samples G5. The temperature cycle was a temperature ramp from room temperature to 1500 °C and then a decrease from 1500 °C to ambient temperature. The heating rates were 20, 10, 5, and 3 °C·min-1 to determine accurately the reduction temperature; the cooling temperature remained constant (20°C·min‑1). In addition, blank samples (Al2O3 powder) were subjected to the same thermal cycles to correct the potential buoyancy effect on the gravimetric measurements.

* 1. Sample characterization

After the heat treatments, epoxy resin was poured into the crucibles to preserve the structure of the entire sample, and the sample was polished under water. Subsequently, these surfaces were coated with a thin film of carbon for the SEM analyses with a Zeiss SUPRATM 55 apparatus. The backscattered electron images were recorded at 15 kV, and energy dispersive X-ray spectrometry (EDX) analyses were conducted to distinguish Ru0 from RuO2. On the samples A and G5 heat-treated for 1 h at 1420 °C, the crystallographic orientation of the Ru0 particles was investigated by electron back-scattered diffraction (EBSD). The X-ray diffraction (XRD) sensitivity is insufficient for detecting small amounts of Ru0 in these samples.

1. Results
   1. Thermodynamic modeling of Ru–O system

Figure 2 presents the calculated predominant domains of ruthenium species as a function of the oxygen pressure and temperature. Because in typical nuclear glass melts log10(p(O2)) is between ‑1 and 0 and the temperature is between 1100 and 1200 °C (grey area in Figure 2), the thermodynamic modeling results predict that in nuclear glasses, pure ruthenium should only occur as RuO2. At the atmospheric oxygen pressure (log10(p(O2) = ‑0.7), the RuO2-to-Ru0 reduction temperature is 1403 °C, and at the elaboration temperature (1200 °C), Ru0 occurs at p(O2) < 10‑1.9 bar (grey-dotted lines).

Figure 2: Existence domains of ruthenium species in Ru–O system. The solid line represents the calculated equilibrium between Ru0 and RuO2. The grey-dotted lines represent the reduction temperature of RuO2 at atmospheric oxygen pressure (1403 °C) and the reduction oxygen pressure of RuO2 at 1200 °C (log10(p(O2)) = ‑1.9).

Moreover, Figure 3 shows the results of the thermodynamics calculations; the speciation of the ruthenium solid phase as a function of the temperature and oxygen partial pressure in the gas phase. In these calculations, the total pressure was fixed to 1 bar, and the oxygen reference state was gaseous oxygen (½ O2). The transition temperatures at which Ru0 occurs corresponds to the reduction temperature Treductionof RuO2 (Table 2) for the conditions in Figure 3. This temperature increases as a function of the oxygen pressure, as already shown in Figure 2.

Figure 3: Evolution of oxygen chemical potential as function of temperature for p(O2) = 0.01, 0.05, 0.2, 0.5, and 1 bar (log(p(O2) = ‑2, ‑1.3, ‑0.7, ‑0.3, 0, respectively) and ptot = 1 bar. The solid and dotted lines correspond to RuO2 and Ru0 stability domains, respectively.

|  |  |  |
| --- | --- | --- |
| p(O2) (bar) | log10(p(O2)) (p in bar) | Treduction (°C) |
| 1 | 0 | 1542 |
| 0.5 | -0.3 | 1483 |
| 0.2 | -0.7 | 1403 |
| 0.05 | -1.3 | 1297 |
| 0.01 | -2 | 1191 |

Table 2: Calculated reduction temperature of RuO2 at different oxygen pressures (ptot = 1 bar).

The thermodynamic calculations in Figure 4 confirm that the ruthenium amount in the gas phase increases with temperature; the formed volatile species are RuO4(g), RuO3(g), RuO2(g), and RuO(g). Regarding sample A conditions (total pressure of 1 bar and oxygen pressure of 0.21 bar), the mainly formed ruthenium volatile species are RuO4 for T < 1002 °C, RuO3 for 1002 °C < T < 1712°C and RuO2 for T > 1712 °C.

Figure 4: Activity of gaseous species in the entire gas phase of Ru–O system; total pressure of 1 bar and oxygen pressure of 0.2 bar.

The composition of the gas phase for p(O2) = 0.2 bar and T = 1403 °C in a closed system with the stoichiometry of RuO2 is listed in Table 3. These results show that in such a case, approximately 16 wt% of the gas phase formed by RuO2 reduction is due to ruthenium volatile species; the remaining 84 wt% is due to dioxygen formation.

|  |  |  |
| --- | --- | --- |
| Gaseous species | Molar % in gas phase | Mass % in gas phase |
| O2 | 96.0 | 83.7 |
| RuO3 | 3.4 | 13.8 |
| RuO2 | 0.4 | 1.5 |
| RuO4 | 0.2 | 1.0 |

Table 3: Detailed composition of gas phase at 1403 °C, p(O2) = 0.2 bar, and ptot = 1 bar.

* 1. Experimental results
     1. RuO2 in air

First, a DTA/TGA investigation was performed on the RuO2 powder in an air atmosphere to compare the experiment and calculated results (Figure 5).

Figure 5: DTA/TGA results of RuO2 powder (sample A) at heating rate of 5 °C·min‑1, the results of the blank samples were subtracted from the original thermogram, and the dotted line represent the RuO2 reduction temperature at 1408 °C.

Figure 6: Evolution of reduction temperature of RuO2 as function of the heating rate.

Heat flow monitoring allows the determination of the reduction temperature of RuO2 to Ru0: 1408 ± 5°C (Figure 5). It can be determined more precisely with the tangent method: 1405 ± 7 °C (Figure 6). The thermal treatments performed in the muffle furnace at 1400, 1410, 1420 and 1500 °C for 1 h confirm this Treduction value: as shown in Figure 7, the first metallic particle is observed in the sample treated at 1410 °C. It can be detected through careful SEM investigations of the cross-sections and EDX analyses.

The non-flat behavior of the heat flow at T < 1400 °C indicates that the system is not frozen before reduction. In addition, the mass monitoring results show two heating stages:

1. at T < Treduction, the slight mass loss is related to the first oxidation and volatilization steps of RuO2 into RuO4(g) and RuO3(g);
2. at T > Treduction, the sudden mass loss is due to the O2 mass loss and volatilization process of RuO3(g) and RuO4(g).

For T < Treduction, the attribution of the mass loss to the volatilization of RuO3(g) and RuO4(g) is confirmed by results obtained with sample A heat-treated in a muffle furnace at 1400°C for 1 h: although no metallic ruthenium can be observed (Figure 7a), the sample  loses approximately 16% of its initial weight.

For T > Treduction, the DTA curve (red peak on Figure 5) indicates that the total mass loss related to the reduction event is 26.5 wt% (grey dotted lines on Figure 5).

In addition, the morphologies of ruthenium were investigated thanks to the samples G5 heat-treated in a muffle furnace. After a heat treatment of 1 h at 1410 °C, the size of the metallic particle is the same as that of the RuO2 particles (Figure 7b). After a heat treatment of 1 h at 1420 °C, Ru0 and RuO2 particles coexist. Nevertheless, the former are scarce and approximately ten times bigger than the RuO2 particles (Figure 7c). After a heat treatment of 1 h at 1500 °C, the entire sample is metallic. More particles are formed, which are smaller than those formed after 1 h at 1420 °C (Figure 7d).

*Figure 7: SEM image of samples A heat-treated in a muffle furnace at 1400 °C (a), 1410 °C (b), 1420 °C (c), and 1500 °C (d) for 1 h. Light-grey particles correspond to Ru0 and dark grey particles to RuO2.*

Figure 8 displays the EBSD results of the Ru0 particles formed after a heat treatment at 1420 °C for 1 h. According to the results, the big particles are monocrystalline, which suggests the involvement of ruthenium volatile species in the growth mechanism of Ru0 particles. This point is discussed in the Discussion Section 4.1. The slight shading at the edges of the particles is assigned to the “edge effect”.

*Figure 8: Secondary electron SEM image (a) and EBSD results of Ru0 particle formed after heat treatment of RuO2 powder (sample A) at 1420 °C for 1 h for directions of x (b), y (c) and z (d).*

* + 1. RuO2 in glass

The only multivalent element present in the glass is iron as impurity (500 wt ppm). The redox couple Fe2O3 /FeO thus controls the evolution of the oxygen pressure of the glass without ruthenium. When RuO2 is added into the glass, the oxygen pressure increases significantly (Figure 9). The oxygen pressure measurement thus indicates that ruthenium in samples G0.5 and in samples G5 is expected in its RuO2 form for the whole investigated temperature range. Between 1150 °C and 1325 °C, the p(O2) of sample G0.5 evolves as well as the calculated equilibrium between RuO2 and Ru0. The increase in the oxygen pressure of the glass for T > 1325 °C may indicate an interaction between ruthenium and the glass melt. The elaboration temperature of the glass is 1350 °C and a new equilibrium between multivalent element couples may be set.

*Figure 9: Oxygen pressure of glass with (*◼*) and without (*●*) ruthenium oxide and thermodynamic calculation of equilibrium between Ru0 and RuO2 (black solid line). The dotted line represents the slope discontinuity in the oxygen pressure of sample G0.5.*

In addition, the samples G5 were heat-treated in the 1200 °C–1550 °C temperature range, analyzed by SEM and compared to the oxygen pressure measurements. According to the results, ruthenium mainly occurs as RuO2 particles for the whole investigated temperature range. However, it is noticeable that a few the first Ru0 particles occur at 1280 °C (Figure 10). Cooling might cause a slight oxidation of the redox species, whereas no additional reduction is expected. Therefore, Ru0 particles (observed at room temperature) are already present at high temperatures. However, at 1280 °C, Ru0 particles are scarce. The SEM images highlight that the Ru0 precipitates represent less than 10‑4 % of the surface occupied by ruthenium particles. At 1250 °C, no Ru0 can be detected, therefore the minor reduction phenomena start between 1250 and 1280 °C. In addition, over 1280 °C, the Ru0 proportion increases with increasing temperature (Figure 10). Over 1400 °C, the Ru0 particles become more numerous and are mainly located near the surface of the glass bath. No oxygen bubble was observed in samples G5 containing Ru0 particles.

In the glass, the morphology of the Ru0 particles exhibits a quite regular shape, and their sizes increase with increasing temperature (Figure 10).

*Figure 10: SEM image of samples G5 heat-treated at 1280 °C (a), 1300 °C (b) and 1500 °C (c) for 1 h. Light-grey particles correspond to Ru0, dark-grey particles to RuO2, and black phase to glass.*

The EBSD results on the Ru0 particles display only one color per particle for any direction (Figure 11). Thus, the Ru0 particles are monocrystalline.

Figure 11: Secondary electron SEM image (a) and EBSD results of RuO2 and Ru0 particles formed after heat treatment of a sample G5 at 1420 °C for 1 h, for directions x (b), y (c), and z (d).

The RuO2 particle morphology exhibits a wide range of sizes: from few nanometers to hundred micrometers. The mean size of these particles increases with increasing temperature and heat treatment duration (Figure 12). Over approximately 1350 °C, very thin needles of ruthenium can be observed, which are distributed in the entire glass (Figure 13). After a heat treatment at 1400 °C for 1 h, a sample G5 was cast, and no needles can be observed. According to Dhargupta and Mukerji [33], these needles can be attributed to solubilized RuO2 in the glass melt and its reprecipitation in the glass matrix. This phenomenon can be amplified by the high amount of Na2O in the glass because Na2O is known to increase the ruthenium solubility [7, 8]. Therefore, these needles are not representative of the high-temperature state (unlike the RuO2 and Ru0 particles) and are just a cooling effect.

*Figure 12: SEM pictures of samples G5 heat-treated at 1300 °C for 1 h (a, a’) and 4 h (b, b’) and at 1500 °C for 1 h (c); dark-grey particles and black phase correspond to RuO2 and glass, respectively.*

*Figure 13: SEM image of thin needles of reprecipitation in sample G5 heat-treated at 1400°C for 1 h.*

1. Discussion
   1. RuO2 reduction in air

The Ru–O Calphad database used for thermodynamic modeling agrees well with the literature data [26]. In addition, the experimental results presented in this paper agree well with both the literature and calculation data. Thus, the RuO2-to-Ru0 reduction (Treduction) can be predicted well, and the calculations allow to attribute the mass loss observed below Treduction in the thermogram to the volatilization of RuO3(g) and RuO4(g) (Figure 4).

However, the high-temperature experiments presented in this paper were performed in an open system, whereas the calculations represent a closed system. These differences explain the small discrepancies between the modeling and experimental results, particularly regarding the amount of volatile species, which was measured in the TGA experiments.

The total mass loss during the reduction step (grey lines on Figure 5) is 13.1 mg which corresponds to 26.5 wt% of the mass of the sample at 1408 °C. The reduction of RuO2 into Ru0 is considered a total reaction. Thus, 93.6 mol% is attributed to O2 off-gas and 6.4 mol% is attributed to the release of Ru-volatile species in the gas phase formed. The proportion of Ru-volatile species is calculated considering RuO3(g) as the only Ru-volatile species and reusing the oxygen released by the reduction reaction to form RuO3(g). This molar percentage of Ru-volatile species agrees quite well with the thermodynamic calculations, which predict that 4 mol% of the gaseous species are composed of ruthenium oxides (Table 3).

In addition, the experimental results suggest an autocatalytic nucleation/growth mechanism for the RuO2-to-Ru0 reduction. Indeed, the temperature dependency of the RuO2 reduction kinetics is characteristic of this kind of mechanism [34-36], as already concluded by Prudenziati *et al.* [36] for an H2 atmosphere. Green *et al.* [37] went further and suggested a disproportionation reaction for the formation of Ru0 films in the heat treatment of RuO2 films at T > 750 °C in a close-vacuum atmosphere. However, neither Prudenziati *et al.* nor Green *et al.* observed any notable morphologic changes of the RuO2 and Ru0 particles. In the present case, because Ru0 particles are monocrystalline and bigger than the initial RuO2 particles, it is assumed that the ruthenium gas phase affects the reduction process in air. Because this phenomenon cannot be observed under reducing conditions and RuO3(g) and/or RuO4(g) are/is easily formed under oxidizing conditions, these two gaseous compounds are assumed to act as intermediates during the RuO2 reduction. Moreover, Ru0 particles are more numerous and smaller at 1500 °C than at 1420 °C. Hence, more Ru0 nuclei can be created at higher temperatures. Therefore, the first step of the Ru0 particle appearance is assumed to be the formation of Ru0 nuclei (Equation 5) for T ≥ Treduction. In addition, after the oxidation of RuO2, RuO3(g) (mainly) is volatilized (Equation 6), the gaseous compound is adsorbed on the metallic ruthenium nuclei (Equation 7), and the direct reduction of RuO3 occurs (Equation 8), which enables the growth of Ru0 particles. The existence of adsorbed RuO3(g) was reported in [38]. The hypothetic mechanism can be expressed as follows (Treduction = 1403 °C, in air):

|  |  |  |
| --- | --- | --- |
|  | (5) | for T ≥ Treduction; |
|  | (6) | for all T under oxidizing conditions and for T ≥ Treduction for Ru:O 1:2 systems; |
|  | (7) | for T ≥ Treduction; |
|  | (8) | for T ≥ Treduction. |

* 1. RuO2 reduction in glass

A minor reduction of RuO2 in glass was experimentally determined to start between 1250 and 1280 °C. From 1280 to 1400 °C, only small and isolated Ru0 particles are formed. Then, from 1400 °C, a more significant reduction phenomenon was highlighted, with a significant amount of Ru0 formed.

In the 1280–1400 °C range, the oxygen pressure of the glass melt is higher than the RuO2/Ru0 equilibrium calculated. In the thermodynamic model, no interaction between the glass and ruthenium is considered, except the p(O2). Therefore, the glass melt must have an impact on the ruthenium redox. To explain this discrepancy, between observations and thermodynamic prediction at T < 1400 °C, two hypotheses are proposed:

1. Iron impurity (Fe2+) may reduce RuO2 in a small amount (Equation 9):

(9)

The maximum content of Fe2+ in samples G5 is around 20 % of the total iron content, or 10‑5 mol of Fe2+. If all Fe2+ reacts with RuO2, a theoretical maximum of 3∙10‑5 mol of Ru0 can be formed, which represents approximately 8∙10-4 mol% of the total amount of ruthenium or 0.05 surface% (assuming vol% is equal to surface%). This value is above the Ru0 proportion determine by SEM image analysis and is thus consistent. However, Ru0 content increases with increasing temperature whereas the reactivity between ruthenium and iron decreases with increasing temperature (because the discrepancy between Fe2O3/FeO and RuO2/Ru0 equilibrium curbs decreases with temperature). This fact leads to consider the influence of iron on the RuO2 reduction reaction only for few Ru0 nuclei at lowest temperature.

1. A disproportionation reaction of RuO2 may occur to form ruthenium volatile species on the one hand and metallic ruthenium on the other hand. The Equation 10 is the example of the disproportionation reaction with RuO4(g).

(10)

This second hypothesis is based on the comparison with phenomena occurring under air conditions. The DTA/TGA of sample A shows that the volatilization of ruthenium gaseous species become significant from 1200 °C. In samples G5 or G0.5, this volatilization reaction is also likely to appear. Since oxygen is less available in glass, RuO3(g) or RuO4(g) can be formed from the reaction of RuO2(s) with itself (Equation 10). This disproportionation reaction can lead to form the scarce Ru0 particles observed between 1280 °C and 1400 °C. This reaction was already mentioned in literature under vacuum conditions [37]. The glass can physically dissolve ruthenium gases. The thin needles observed (Figure 13) can thus be precipitation of ruthenium gases and / or dissolved RuO2. Because glass can trap ruthenium gases, the yield of the disproportionation reaction is not high and only few and small particles of Ru0 are observed in glass until 1400 °C.

At T > 1400 °C, RuO2 can decompose because of oxygen pressure and temperature conditions, according the Equation 11:

(11)

In addition, regarding the growth of RuO2 particles, as already proposed in [39-41], an Oswald ripening mechanism can explain the notable size increase of RuO2 particles with increasing time and temperature, as well as their monocrystalline feature. This hypothesis is supported by the occurrence of reprecipitated needles in some samples G5, which illustrates that ruthenium is partly dissolved in the glass. Ruthenium can be dissolved as RuO2 or as RuO3(g) or RuO4(g) owing to the disproportionation reaction.

Regarding the growth of Ru0 particles, the fact that Ru0 particles are monocrystalline and become bigger with increasing temperature can also be explained by the existence of dissolved ruthenium in the glass (as a gas or as RuO2). Even if solid RuO2 is more likely to become reduced than dissolved ruthenium, the permanent equilibrium between both forms may allow dissolved RuO2 to be reduced on Ru0 nuclei, which were previously formed. According to the mechanism proposed for samples A, a hypothesis of growth mechanism is proposed with the example of dissolved RuO2 (1250°C < Treduction < 1280°C in this glass):

|  |  |  |
| --- | --- | --- |
|  | (12) | for all T; |
|  | (13) | for T ≥ Treduction; |
|  | (14) | for T ≥ Treduction. |

1. Conclusion

The comparison of the theoretical calculation and experimental results presented in this paper for the reduction of RuO2 into Ru0 shows that:

1. In air, the experimental and calculated reduction temperatures (1405 and 1403 °C, respectively) are in very good agreement. Thermodynamic calculations are a powerful and quick tool for predicting quantitatively the equilibrium state of the Ru-O system under any conditions. In addition, the experiments and calculations show that the RuO2 reduction is a complex phenomenon that involves volatilization reactions. The experimental results lead to the assumption that the formation of Ru0 particles results from an autocatalysis and that they grow owing to the ruthenium gas phase, leading to monocrystalline Ru0 particles bigger than initial RuO2 particles.
2. Regarding the behavior of ruthenium in the studied glass, free of multivalent element, the comparison between calculations and experimental results shows that minor reduction phenomena start at quite low temperatures (1280 °C). These phenomena result in the appearance of a few small particles of Ru0. This minor reduction, which is not predicted by thermodynamic calculation, is assumed to be due to the interactions between ruthenium and glass through either redox reaction with iron impurity or disproportionation reaction of RuO2. At T > 1400 °C, a more significant reduction phenomenon starts. This one is attributed to the reduction of RuO2 in Ru0 due to oxygen pressure and temperature conditions, as predicted by thermodynamic calculations. Based on the proposed reduction mechanism in air, the growth of Ru0 is supposed to involve ruthenium species dissolved in the glass.

As a conclusion, Calphad thermodynamic databases allow to predict the major behavior of ruthenium in the glass. However, it does not allow to predict the minor reduction due to interactions between ruthenium and glass. Thanks to a better control of the oxygen pressure, this minor reduction is not expected in glasses containing multivalent species at a significant level.

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**References**

1. Kleykamp H., Paschoal J.O., Pejsa R., Thümmler F. (1985). *Composition and structure of fission product precipitates in irradiated oxide fuels: correlation with phase studies in the Mo-Ru-Rh-Pd and BaO-UO2-ZrO2-MoO2 systems.* Journal of Nuclear Materials, **130**: p. 426-433. <https://doi.org/10.1016/0022-3115(85)90329-0>
2. Kleykamp H. (1990). *Post-irradiation examinations and composition of the residues from nitric acid dissolution experiments of high-burnup LWR fuel.* Journal of Nuclear Materials, **171**: p.181-188. <https://doi.org/10.1016/0022-3115(90)90364-S>
3. Adachi T., Ohnuki M., Yoshida N., Sonobe T., Kawamura W., Takeishi H., Gunji K., Kimura T. Suzuki T., Nakahara Y., Muromura T., Kobayashi Y., Okashita H., Yamamoto T. (1990). *Dissolution study of spent PWR fuel: dissolution behavior and chemical properties of insoluble residues.* Journal of Nuclear Materials, **174**: p. 60-71. <https://doi.org/10.1016/0022-3115(90)90421-I>
4. Matsui T., Yamamoto T., and Naito K. (1990). *Dissolution of a simulated fission-produced noble metal alloy in nitric acid solution at 383 K.* Journal of Nuclear Materials, **174**(1): p. 16-21. <https://doi.org/10.1016/0022-3115(90)90416-K>
5. Boucetta H., Podor R., Stievano L., Ravaux J., Carrier X., Casale S., Gossé S., Monteiro A., Schuller S. (2012). *Mechanism of RuO2 crystallization in borosilicate glass: an original in situ ESEM approach.* Inorganic Chemistry, **51**(6): p. 3478-89. <https://doi.org/10.1021/ic202156y>
6. CEA (2009). *Nuclear Waste Conditioning*, in *DEN monograph*.
7. Mukerji J. (1972). *Behavior of Ruthenium in Glass.* Ind. Eng. Chem. Prod. Res. Develop., **11**(2): p. 178-183. <https://doi.org/10.1021/i360042a010>
8. Mukerji J., Biswas S.R. (1967). *Solubility of ruthenium in soda-silica glass.* Cent. Glass Ceram. Res. Inst. Bull. **14**(2): p. 30-34.
9. Biswas S.R., Mukerji J. (1968). *Solubility of ruthenium in silicate and phosphate glass.* Cent. Glass Ceram. Res. Inst. Bull. **15**(4): 99-103.
10. Borisov A., Nachtweyh K. (1998). *Ru solubility results in silicate melts: experimental results in oxidizing region*, in *Lunar and Planetary Science XXIX*.
11. Capobianco C.J., Hervig R.L. (1996). *Solubility of Ru and Pd in silicate melts: the effect of melt composition*, in *Lunar and Planetary Science Conference XXVII*.
12. Palanisamy P., Sarma D.H.R., Vest R.W. (1989). *Solubility of RuO2 in lead borosilicate glasses.* J. Am. Ceram. Soc. **72**(9): p. 1755-1756. <https://doi.org/10.1111/j.1151-2916.1989.tb06321.x>
13. Shuto H., Okabe T.H., Morita K. (2011). *Ruthenium Solubility and Dissolution Behavior in Molten Slag.* Materials Transactions, **52**(10): p. 1899-1904. <https://doi.org/10.2320/matertrans.M-M2011821>
14. Schreiber H.D., Settle F.A., Lynne Jamison P., Eckenrode J.P., Headley G.W. (1986). *Ruthenium in glass-forming borosilicate melts.* Journal of the Less-Common Metals, **115**: p. 145-154. <https://doi.org/10.1016/0022-5088(86)90379-6>
15. Demin A.V., Fedorova M.I., Matyunin Y.I. (1996). *Localization of platinum-group elements and technetium and the solidification of high-level liquid wastes.* Atomic Energy, **80**(3): p. 178-181. <https://doi.org/10.1007/BF02414804>
16. Cobb W.T., Hrma P. (1991). *Behavior of RuO2 in a glass melt*, in *Nuclear Waste Management IV,* p. 233-237.
17. Gong W., Lutze W., Matlack K.S., Pegg I.L. (2009). *Testing and modelling the behaviour of platinoids during vitrification of high level radioactive wast: Part 3.* Glass Technology: European Journal of Glass Science and Technology, Part A, **50**(2): p. 95-107.
18. Hanotin C., Puig J., Neyret M., Marchal P. (2016). *Platinum group metal particles aggregation in nuclear glass melts under the effect of temperature.* Journal of Nuclear Materials, **477**: p. 102-109. <https://doi.org/10.1016/j.jnucmat.2016.04.033>
19. Arblaster J.W. (2016). *Selected Electrical Resistivity Values for the Platinum Group of Metals Part III: Ruthenium and Osmium.* Johnson Matthey Technology Review, **60**(3): p. 179-185. <https://doi.org/10.1595/205651316x691618>
20. Ryden W.D., Lawson A.W., C.C. Sartain (1968). *Temperature dependence of the resistivity of RuO2 and IrO2.* Physics Letters A, **26**(5): p. 209-210. <https://doi.org/10.1016/0375-9601(68)90126-6>
21. Guyer E.M. (1933). *The electrical behavior of glass at room temperature*. Journal of the American Ceramic Society, **16**(1-12): p. 607-618. <https://doi.org/10.1111/j.1151-2916.1933.tb19268.x>
22. Simonnet C. (2004). *Conductivité électrique des verres et fontes d'oxydes : effet de l'incorporation de particules de RuO2*. PhD, Montpellier 2.
23. Bell W.E., Tagami M. (1963). *High-Temperature Chemistry of the Ruthenium-Oxygen System.* The Journal of Physical Chemistry, **67**(11): p. 2432-2436. <https://doi.org/10.1021/j100805a042>
24. Brunetti B., Scardala P., Piacente V. (2004). *Dissociation pressure and standard dissociation enthalpy of RuO2.* Materials Chemistry and Physics, **83**(1): p. 145-149. <https://doi.org/10.1016/j.matchemphys.2003.09.012>
25. Jacob K.T., Mishra S., Waseda Y. (2000). *Refinement of the thermodynamic properties of ruthenium dioxide and osmium dioxide.* Journal of the American Ceramic Society, **83**(7): p. 1745-1752. <https://doi.org/10.1111/j.1151-2916.2000.tb01459.x>
26. Gossé S., Bordier S., Guéneau C., Brackx E., Domenger R., Rogez J. (2018). *Thermodynamic assessment of the rhodium-ruthenium-oxygen (Rh-Ru-O) system.* Journal of Nuclear Materials, **500**: p. 252-264. <https://doi.org/10.1016/j.jnucmat.2017.12.034>
27. Okamoto Y., Shiwaku H., Nakada M., Komamine S., Ochi E., Akabori M. (2016). *REDOX state analysis of platinoid elements in simulated high-level radioactive waste glass by synchrotron radiation based EXAFS.* Journal of Nuclear Materials, **471**: p. 110-115. <https://doi.org/10.1016/j.jnucmat.2016.01.008>
28. Pinet O., Mure S. (2009). *Redox behavior of platinum-group metals in nuclear glass.* Journal of Non-Crystalline Solids, **355**(3): p. 221-227. <https://doi.org/10.1016/j.jnoncrysol.2008.11.002>
29. Lukas H.L., Fries S.G., Sundman B. (2007). *Computational Thermodynamics: The Calphad Method*. Cambridge University Press.
30. Gossé S., Schuller S., Guéneau C. (2010). *Thermodynamic modelling of the Pd-Te-Ru system for nuclear waste glasses application,* in *MRS Symposium AA*, **1265**. <https://doi.org/10.1557/PROC-1265-AA03-04>
31. Gossé S., Guéneau C. (2011). *Thermodynamic assessment of the palladium-tellurium (Pd-Te) system*. Intermetallics, **19**(5): p.621-629. <https://doi.org/10.1016/j.intermet.2010.12.014>
32. Schaeffer H.A., Frey T., Löh I., Baucke F.G.K. (1982). *Oxidation state of equilibrated and non-equilibrated glass melts.* Journal of Non-Crystalline Solids, **49**(1-3): p. 179-188. <https://doi.org/10.1016/0022-3093(82)90117-X>
33. Dhargupta K.K., Mukerji J. (1968). *Solubility Dependence of Ruthenium Volatilisation from Glass.* Transactions of the Indian Ceramic Society, **27**(1): p. 123-129. <https://doi.org/10.1080/0371750X.1968.10855641>
34. Kung, H.H., *Reduction of oxides*, in *Transition metal oxides: surface chemistry and catalysis*. 1989, Elsevier. p. 91-109.
35. Rodriguez J.A., Hanson J.C., Frenkel A.I., Kim J.Y., Pérez M. (2002). *Experimental and theoretical studies on the reaction of H2 with NiO: role of O vacancies and mechanism for oxide reduction.* Journal of American Chemical Society, **124**(2): p. 346-354. <https://doi.org/10.1021/ja0121080>
36. Prudenziati M., Morten B., Travan E. (2003). *Reduction processof RuO2 powders and kinetics of their re-oxidation.* Materials Science and Engineering: B, **98(2)**: p. 167-176. <https://doi.org/10.1016/S0921-5107(03)00049-7>
37. Green, M.L., Gross M.E., Papa L.E., Schnoes K.J., Brasen D. (1985). *Chemical vapor deposition of ruthenium and ruthenium dioxide films.* Journal of the Electrochemical Society, **132**(11): p. 2677-2685. <https://doi.org/10.1149/1.2113647>
38. Eichler B., Zude F., Trautman N., Fan W., Herrmann G. (1992). *Volatilization and deposition of ruthenium oxides in a temperature gradient tube.* Radiochimica Acta, **56**(3): p. 133-140. <https://doi.org/10.1524/ract.1992.56.3.133>
39. Nakano T., Suzuki K., Yamaguchi T. (1994). *Analysis of interaction between RuO2 and glass by growth of RuO2 particles in glass.* Journal of Adhesion, **46**(1-4): p. 131-144. <https://doi.org/10.1080/00218469408026655>
40. Pflieger R., Lefebvre L., Malki M., Allix M., Grandjean A. (2009). *Behaviour of ruthenium dioxide particles in borosilicate glasses and melts.* Journal of Nuclear Materials, **389**(3): p. 450-457. <https://doi.org/10.1016/j.jnucmat.2009.02.034>
41. Prabhu A.N., Vest R.W. (1975). *Investigation of microstructure development in RuO2-lead borosilicate glass thick films*, in Kuczynski G.C. (eds) *Sintering and Catalysis*. Materials Science Research, Springer, **10**: p. 399-408. <https://doi.org/10.1007/978-1-4684-0934-5_30>

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Description générée automatiquement

Figure 1: SEM images of typical simulated nuclear glass. Grey needles and white round particles are RuO2 particles and Pd–Te beads, respectively.

Une image contenant capture d’écran

Description générée automatiquement

Figure 2: Existence domains of ruthenium species in Ru–O system. The solid line represents the calculated equilibrium between Ru0 and RuO2. The grey-dotted lines represent the reduction temperature of RuO2 at atmospheric oxygen pressure (1403 °C) and the reduction oxygen pressure of RuO2 at 1200 °C (log10(p(O2)) = ‑1.9).



Figure 3: Evolution of oxygen chemical potential as function of temperature for p(O2) = 0.01, 0.05, 0.2, 0.5, and 1 bar (log(p(O2) = ‑2, ‑1.3, ‑0.7, ‑0.3, 0, respectively) and ptot = 1 bar. The solid and dotted lines correspond to RuO2 and Ru0 stability domains, respectively.

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Figure 4: Activity of gaseous species in the entire gas phase of Ru–O system; total pressure of 1 bar and oxygen pressure of 0.2 bar.

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Figure 5: DTA/TGA results of RuO2 powder (sample A) at heating rate of 5 °C·min‑1, the results of the blank samples were subtracted from the original thermogram, and the dotted line represent the RuO2 reduction temperature at 1408 °C.



Figure 6: Evolution of reduction temperature of RuO2 as function of the heating rate.

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*Figure 7: SEM image of samples A heat-treated in a muffle furnace at 1400 °C (a), 1410 °C (b), 1420 °C (c), and 1500 °C (d) for 1 h. Light-grey particles correspond to Ru0 and dark grey particles to RuO2.*

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*Figure 8: Secondary electron SEM image (a) and EBSD results of Ru0 particle formed after heat treatment of RuO2 powder (sample A) at 1420 °C for 1 h for directions of x (b), y (c) and z (d).*

Une image contenant vert, assis, sombre, rue

Description générée automatiquement

*Figure 9: Oxygen pressure of glass with (*◼*) and without (*●*) ruthenium oxide and thermodynamic calculation of equilibrium between Ru0 and RuO2 (black solid line). The dotted line represents the slope discontinuity in the oxygen pressure of sample G0.5.*

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Description générée automatiquement

*Figure 10: SEM image of samples G5 heat-treated at 1280 °C (a), 1300 °C (b) and 1500 °C (c) for 1 h. Light-grey particles correspond to Ru0, dark-grey particles to RuO2, and black phase to glass.*

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Description générée automatiquement

Figure 11: Secondary electron SEM image (a) and EBSD results of RuO2 and Ru0 particles formed after heat treatment of a sample G5 at 1420 °C for 1 h, for directions x (b), y (c), and z (d).



*Figure 12: SEM pictures of samples G5 heat-treated at 1300 °C for 1 h (a, a’) and 4 h (b, b’) and at 1500 °C for 1 h (c); dark-grey particles and black phase correspond to RuO2 and glass, respectively.*



*Figure 13: SEM image of thin needles of reprecipitation in sample G5 heat-treated at 1400°C for 1 h.*