KNUDSEN CELL-MASS SPECTROSCOPIC STUDIES OF STRONTIUM VAPOUR PRESSURES OVER STRONTIUM OXIDE/URANIUM DIOXIDE MIXTURES AND SOLID SOLUTIONS

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ABSTRACT

High temperature, Knudsen cell-mass spectroscopic (KC-MS) experiments were performed to determine the volatility of strontium oxide dissolved in UO_2 fuel. KC-MS experiments were carried out with finely ground and pre-heated mixtures of SrO and UO_2 and "solid solutions" of SrO in UO_2, prepared using the sol-gel method. It was found that the main strontium gaseous species over these samples was Sr atoms. The KC-MS experiments showed that the vapour pressures of Sr over pre-heated-mixtures of SrO and UO_2, at high temperatures, were similar to those over pure SrO. The vapour pressures of Sr, over "sol-gel prepared solid solutions" of compositions SrO:UO_2 equal to1:100 and 2:100 were similar to each other and to those reported over pure SrO by Lamoreaux et al. (for congruent vapourization); but were lower than those over pure SrO observed in this work, and over $SrUO_3$ reported by Huang et al. and Yamawaki et al.

1. INTRODUCTION

The release of Sr under some postulated loss of coolant events in a CANDU power plant is a significant issue for the estimation of public, operator and equipment doses [1]. In spite of the importance of Sr in safety analyses, very little direct experimental information is available about Sr release in the results of fission product release and transport (FPRT) tests carried out for reactor safety studies. The main reason for the relative scarcity of experimental data about strontium release in FPRT tests is the fact the main radioactive isotope of strontium (^{90}Sr) is a beta emitter and not a gamma emitter, and in the majority of the FPRT tests gamma spectrometry is used to monitor the FPs release (e.g., see the paper by Dickson et al. in these proceedings [2]). Information about the Sr release in the FPRT tests is often inferred from post-test beta counting analysis of solutions and condensates.

The oxidation state of FP strontium in irradiated nuclear fuel is expected to be the same as in SrO [1]. It has been suggested that SrO can form solid solutions with UO_2. According to Kleykamp, SrO can form solid solution with UO_2 up to 12 atom% Sr [3]. Therefore, it was decided to investigate the effects of the postulated solubility of SrO in the UO_2 on its volatility. Knudsen cell-mass spectroscopic (KC-MS) experiments were performed on mixtures and "solid solutions" of SrO in UO_2 to determine the volatility of strontium in these samples. KC-MS was used because it is possible to measure vapour pressures at high temperatures of non-volatile ceramic solids, such as SrO and UO_2, using this technique. This paper presents the results of these KC-MS experiments.

2. EXPERIMENTAL

2.1 Materials

SrO was obtained from Pfaltz & Bauer Inc. (Stamford, Conn. USA 06902). It was a fine powder, light grey in colour, and was used without further purification. Uranium dioxide used was obtained from CANDU® fuel pellets (0.7 wt% ^{235}U). The fuel pellet was broken and the central part of the pellet was used for the experiments. The central part of the pellet was used, as it should have suffered minimum oxidation by the atmospheric oxygen and is believed to have a composition close to $UO_{2.00}$ [4-6]. The fuel pieces from the central part of the pellet were crushed and sieved, under an inert atmosphere, to obtain particle sizes between 25 and 125 μm. SrO and UO_2 powders were mixed to prepare samples for KC-MS experiments. The UO_2 stock, and the SrO and UO_2 mixtures were kept in an N_2-filled desiccator to prevent oxidation by air [6]. In addition, KC-MS experiments were also carried out with two "solid solutions" of SrO in UO_2 prepared using the sol-gel process, as described below.

"Solid solutions" of SrO in UO_2, using sol-gel method, were prepared for two concentrations of strontium in UO_2 (1 and 2 Sr-metal atom% basis). Measured volumes of strontium nitrate (concentration 0.125 mol/L) and uranyl nitrate (concentration 0.5 mol/L) solutions were mixed to give the desired atom% of Sr and U. Aqueous ammonia (concentration ~25% NH_3) was added to the uranium-strontium nitrate solution to precipitate ammonium diuranate along with co-precipitated strontium [7]. The resulting precipitate was filtered and washed with dilute aqueous ammonia. The resulting precipitate was air-dried at about 100°C for 1 h, and then converted to strontium-doped U_3O_8 by heating in air at 900°C for ~20 h. This solid was reduced to SrO-doped UO_2 by heating in a flowing H_2/Ar mixture (2% H_2) for ~ 16 h at ~850°C [7 and references therein]. The concentrations of Sr and U in the two "solid solution" samples, prepared using the sol-gel method, were determined using ICP-MS (inductively coupled plasma-mass spectroscopy). The ICP-MS results showed that the Sr-metal atom% in the two samples prepared by the sol-gel method was 1.12±0.05% and 2.12±0.05%, respectively.

2.2 X-ray Diffraction

The XRD patterns of SrO and selected SrO:UO_2 mixtures were recorded using a diffractometer consisting of a Rigaku RU-200BH generator, Rigaku CN2155D5 goniometer with specimen rotation and a copper anode operated at a power of 7.5 kW. The powder sample used for analysis was suspended in Vaseline (White Petroleum Jelly) and the Vaseline suspension was smeared on a glass slide so that the XRD pattern could be recorded. The pattern was excited using Cu $K\alpha_1$ X-rays with $\lambda = 1.54056$ Å (1 Å = 1 nm).

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2.3 Knudsen Cell-Mass Spectroscopy

The Knudsen cell-mass spectrometer system used in this work has been described elsewhere [4,6,7]. The Knudsen cells used were constructed from tantalum metal. Each cell had an inner diameter (i.d.) of 12.7 mm, length of 34.0 mm, and an orifice size of ~0.6 mm. The solid sample was placed in a thin-walled tantalum crucible (i.d. ~7.4 mm, wall thickness ~ 0.4 mm). The cell, containing the crucible with the sample, was placed in the Knudsen cell chamber and the system was pumped overnight (~ 16 h), to degas the sample and establish a high vacuum, before starting the experiment. The cell was inductively heated using a Radyne 17 kW power supply and the temperature of the cell was monitored using pyrometers.

The mass spectra of the gases effusing out of the Knudsen cell were recorded after the cell reached the desired temperature. Volatile species effusing out of the heated Knudsen cell, through a small orifice in the cell cap, were ionized in a crossbeam deflector by electron bombardment. The mass spectra were recorded for spectral region 10-550 amu/z (atomic mass per unit charge). The data points were collected with a step size = 0.1 amu/z. Before each signal scan was recorded, a background scan was collected (shutter closed). The intensities of the peaks observed in the mass spectra were obtained by subtracting the background spectrum from the corresponding signal-scan spectrum. The sensitivity of the mass spectrometer, on the day of the experiment, was determined by comparing the intensities of the N_2^+, O_2^+ and Ar^+ ion peaks in the background spectra with the intensities of these peaks in the spectra recorded for the silver primary standard.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction

The XRD diffraction patterns were recorded for three SrO/UO_2 mixtures, of nominal composition SrO:UO_2 = 1:100 (mole ratio) used in the 1st series of KC-MS experiments (see below, Section 3.2.3). The samples analyzed using XRD were obtained by grinding:

a) SrO/UO_2 mixture (in the mole ratio of 1:100) at room temperature;
b) SrO/UO_2 mixture (in the mole ratio of 1:100) heated to 850°C for 4 h; and
c) solid left in the cell after a KC-MS experiment with a sample of initial composition: SrO:UO_2 = 1:100.

The XRD patterns of the SrO/UO_2 mixtures were recorded for 2-theta values between 10° and 120°. Figure 1 shows the XRD pattern observed for mixture (a). The patterns of the three XRD samples were nearly identical with that reported for UO_2 [5,8] and did not show the peaks seen in the pattern for pure SrO (Powder Diffraction File (PDF) # 06-0520 in reference [8]). One may attribute the absence of SrO signal in the XRD of SrO/UO_2 powders heated to high temperatures (i.e., samples (b) and (c)) to the formation of "solid solutions" of SrO and UO_2. However, it is unlikely that a "solid solution" was formed in sample (a). The XRD pattern of this sample was recorded after grinding the two solids together at room temperature and the sample was not heated. The absence of a SrO signal in the XRD pattern of this sample suggests that the XRD method, as used in the present work, is not sufficiently sensitive to detect the presence of SrO in UO_2 at a concentration of about 1%. It may be mentioned here that both SrO and UO_2 solids have a similar lattice structure (i.e., face-centred-cubic) and have same space group ($Fm\bar{3}m$) but have slightly different unit cell parameters. The cell dimension of SrO is 5.1396 Å, compared to 5.4704 Å for UO_2 [8]. As the scattering cross section of U atoms for X-rays is much higher than that of Sr atoms, it makes it difficult to detect, using XRD, small amounts of SrO in the presence of UO_2.

The XRD results showed that the KC-MS samples contained uranium as UO_2, and the uranium in the samples has not suffered any significant oxidation due to its exposure to air, for short times during sample handling.

3.2 Knudsen Cell-Mass Spectroscopy

3.2.1 Appearance Potentials

The Knudsen cell-mass spectra of SrO were recorded with varying electron energy (eV) to determine the optimum electron energy for creating strontium ions for recording the spectra of this system. A value of 35 eV was selected to record the mass spectra in this system from the results shown in this figure. The appearance potential values of Sr^+ and Sr^{2+} ions obtained here (5.4±0.3 eV and 15.6±1.5 eV, respectively) agreed with the literature values [9].

3.2.2 Calculation of Vapour Pressures

The vapour pressures of the parent species of ions seen in Knudsen cell-mass spectroscopic experiments are calculated using the equation [4,6]:

$$p_i = I_i T / (\sigma_i \gamma_i \eta_i k_{Ag} f s) \qquad (1)$$

where:

I_i = signal intensity of the cation formed from the ionization of the species,
T = temperature/K,
σ_i = ionization cross-section of the precursor to the ion,
γ = the mass dependence of the quadrupole analyzer and electron multiplier efficiency for the mass of the ion,
η_i = isotopic abundance,
k_{Ag} = calibration constant, derived from a calibration experiment with the silver primary standard,
f = correction for the area of the orifice of the cell (relative to that in the silver experiment), and
s = correction for the sensitivity of the instrument on the day of the experiment.

The accuracy of the vapour pressures determined using Knudsen cell-mass spectroscopy depends on the nature of the chemical system being studied and the uncertainties in the values of the various terms in Equation (1). The values of the ionization cross-sections (σ_i) and isotopic abundances (η_i) are obtained from the literature. The values of all other terms in equation (1) are determined experimentally. In this work, the value for the ionization cross-section of strontium, i.e.,

$$Sr + e^- \rightarrow Sr^+ + 2e^- \qquad (2)$$

for the 35 eV electrons (the electron energy in this work),was obtained from the paper of Margreiter et al. [10], and the value used in this work was 9.4×10^{-20} m^2.

3.2.3 Vapour Pressures

Lamoreaux et al. [11] have reported, from an extensive review of the literature, that the strontium vapour species, over solid SrO, under neutral or slightly oxidizing conditions, consist mainly of Sr(g). The high temperature vaporization of SrO under these conditions is accompanied by its decomposition:

$$SrO(s) \rightarrow Sr(g) + O(g) \qquad (3)$$

The strontium species seen in the mass spectra recorded here were Sr^+ and very small amounts of Sr^{2+}. The SrO^+ ion peak was not observed in the mass spectra recorded in the present experiments. SrO molecules, if present in the gases effusing out of the Knudsen cell in the experiments described here, could have undergone some fragmentation during their collisions with the electrons (used to create ions for recording the mass spectra). But, it is very unlikely that the collisions with electrons would have fragmented all of the SrO molecules without creating any SrO^+. We believe that the fraction of the SrO(g) in the vapour phase over SrO(s), at high temperatures (> 1700 K) in the experiments described here, is probably less than 5%. Vapour pressures of Sr(g) over different samples were calculated from the intensities of the Sr^+ ions using equation (1).

Three separate series of KC-MS experiments were carried out to determine the volatility of SrO in the presence of UO_2 in the present study. In all three series, peaks of three uranium species, UO_2^+, UO^+ and U^+, were observed at high temperatures, but the UO_3^+ peak was not seen in any of the spectra. This indicates that uranium in the KC-MS samples was present essentially as UO_2, and did not suffer any significant oxidation during its exposure to air during the transfer of the sample into the Knudsen cell [7]. This observation is consistent with the XRD results discussed above which showed that the KC-MS samples contained UO_2 and that no other higher oxide of uranium were present in the KC-MS samples. The results for the three series of KC-MS experiment are summarized below.

The 1st series of KC-MS experiments was completed before the abstract for this conference was written. The KC-MS experiments in this series were carried out with SrO and UO_2 mixtures of three compositions, with SrO:UO_2 ratios equal to 1:1, 1:10, and 1:100. The mixtures were pre-heated, in the Knudsen cell, at about 700 K and 1100 K for a few hours, before the KC-MS experiments at higher temperatures, to promote the formation of "solid solution" of SrO in UO_2. It was observed that the vapour pressures of Sr(g) over samples of mixtures of SrO and UO_2

mixtures with compositions equal to 1:1 and 1:10 were not much different from the vapour pressures of Sr(g) over SrO.

Large numbers of experiments were performed with mixtures/"solid solutions" of composition SrO:UO_2 equal to1:100, in this series of experiments, as the Sr concentration in the irradiated CANDU fuel is less than 1% [12]. Although the results for the individual samples showed linear relationships (as Clapeyron-Clausius plots [13]) with very similar slopes, there were considerable variations in the vapour pressure results for the different samples. It was believed that the most probable cause of the scatter in the observed vapour pressure values of the KC-MS experiments was low signal/noise ratio (i.e., sensitivity) of the mass spectrometer used in these experiments. In order to increase the signal/noise ratio (i.e., sensitivity) of the mass spectrometer system, it was decided to replace the detector of the mass spectrometer with a new and more sensitive detector, before attempting additional experiments. The experiments in the 2nd and 3rd series were performed with a new detector in the MS. The sensitivity (signal/noise ratio) of the MS system in the 2nd and 3rd series was higher by a factor of about 5 compared to that in the 1st series.

The 2nd series experiments were carried out with SrO and UO_2 mixtures of three compositions, with SrO:UO_2 ratios equal to 0.5:100, 1:100 and 2:100. SrO and UO_2 mixtures were thoroughly mixed by grinding under N_2 atmosphere. The samples were pre-heated for a couple of hours to facilitate the formation of "solid solution" of SrO with UO_2, before recording the KC-MS (~1 h at 800 K and ~1 h 1100 K). No difference was observed in the vapour pressures of the three samples of SrO/UO_2, or between the vapour pressures of the three samples of SrO/UO_2 and SrO.

The 3rd series experiments were carried out with SrO and UO_2 "solid solutions" prepared using the sol-gel method [7]. Samples used were of two compositions, with SrO:UO_2 ratios equal to about 1.1:100 and 2.1:100. The Sr vapour pressures observed over the two solids are shown in Figure 2. This figure also contains the total vapour pressures of strontium species over SrO, observed in this work, and those calculated from the paper of Lamoreaux et al. (for the congruent vapourization of SrO, i.e., Figure 14 in their paper [11]). This figure also shows Sr vapour pressures over $SrUO_3$ (in excess UO_2) measured by Huang et al. [14] and Yamawaki et al. [15] for comparison purposes. The Sr vapour pressures over $SrUO_3$ reported by Huang et al. and Yamawaki et al. are higher than those over the "sol-gel prepared SrO UO_2 solid solutions" but are close to those observed over SrO in this work, Figure 2. It may be noted here that the attempts to synthesize $SrUO_3$ have not been fully successful – see papers by Cordfunke and IJdo [16] and Huang et al. [14] for the difficulties encountered in the synthesis of $SrUO_3$. The vapour pressure of Sr over the "two sol/gel prepared solid solutions" of SrO in UO_2 are lower than those observed over pure SrO (in this work) but there is no measurable difference between the vapour pressures of the two "solid solution" samples containing 1% and 2% SrO in UO_2, as was observed for La-species vapour pressure over lanthanum oxide/ UO_2 solid solutions [7]. It may be noted here that the ionic radii of U^{4+} (1.00 Å) and Sr^{2+} (1.27 Å) are too dissimilar to form solid solutions according to the well-known Goldschmidt 15% rule. (The Goldschmidt rule states that ions of radii within 15% of each other can form solid solutions.).

4. SUMMARY AND CONCLUSIONS

Knudsen cell-mass spectroscopic experiments were carried out with samples of SrO, UO_2 mixtures of compositions (SrO:UO_2) equal to 100:100, 10:100, 2:100, 1:100 and 0.5:100, and sol-gel prepared "solid solutions" of compositions about 2:100 and 1:100.

The KC-MS results suggest that Sr vapour pressures over "sol-gel prepared solid solutions" of SrO and UO_2, of composition SrO:UO_2 equal to1:100 and 2:100 are similar to each other, and to those reported over pure SrO by Lamoreaux et al. (for congruent vapourization). The vapour pressures of Sr over "solid solutions" of SrO in UO_2 are lower than those over SrO (as observed in this work) and $SrUO_3$ (as reported by Huang et al. and Yamawaki et al).

The vapour pressure of strontium in SrO in UO_2 system is very sensitive to the oxidation potential of the system as can be seen by the results reported by Lamoreaux et al. for different "oxygen concentrations" [11]. Thermodynamic calculations (by W. Thompson) indicate that Sr pressure decreases by a factor of two if the uranium oxidation state in SrO/UO_2 mixtures changes from $UO_{2.0001}$ to $UO_{1.9999}$ [17]. Future studies should be carried out under more controlled oxygen potential conditions to further investigate this observation.

The nature of the Sr-U-O phases in fuel, formed due to the formation of FP strontium, will be a function of the oxidation state of uranium [16,18,19]. As discussed by Fujino et al. [19], if FP strontium is formed, the fuel lattice will probably be UO_{2+x} and the formation of a solid solution of SrO in pure UO_2 (or formation of $SrUO_3$) may not be relevant except as a limiting case. Therefore, future studies of SrO in UO_2 should be carried out as a function of uranium oxidation state. Other structure sensitive spectroscopic techniques such as vibrational spectroscopy (i.e., Raman scattering and infrared absorption) should be used to investigate the phases formed in the $(U,Sr)O_{2+x}$ systems.

5. ACKNOWLEDGMENTS

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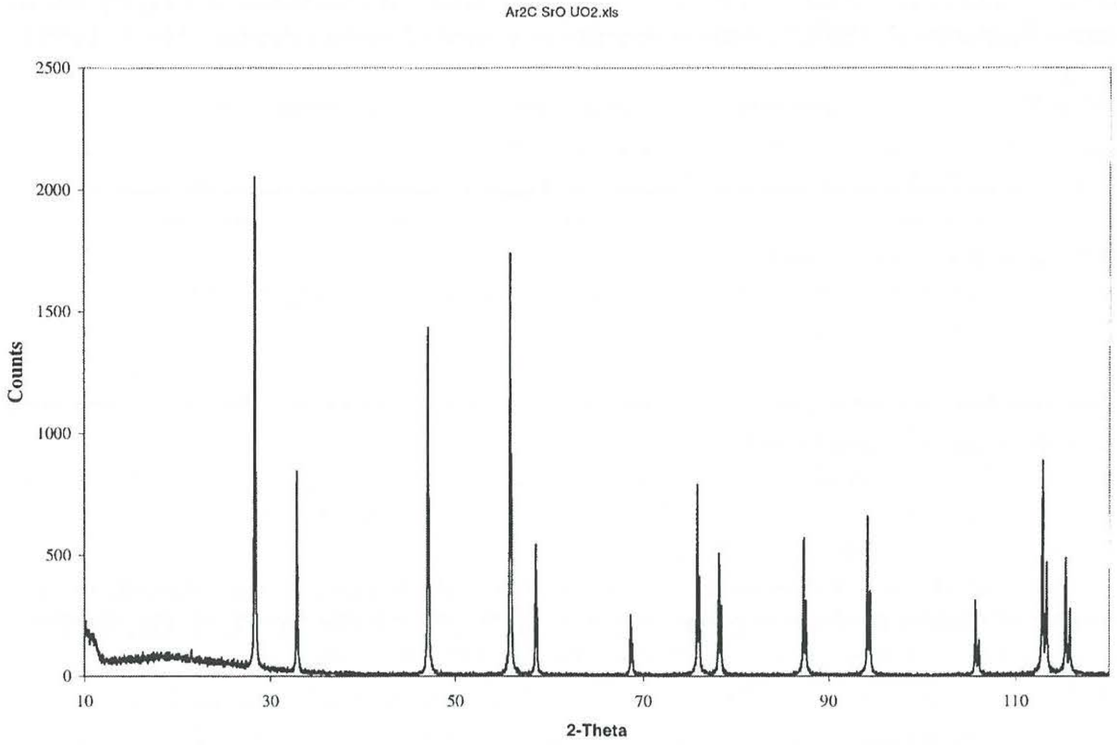

Figure 1: XRD Pattern of a SrO:UO$_2$ Mixture of Composition SrO:UO$_2$ = 1:100.

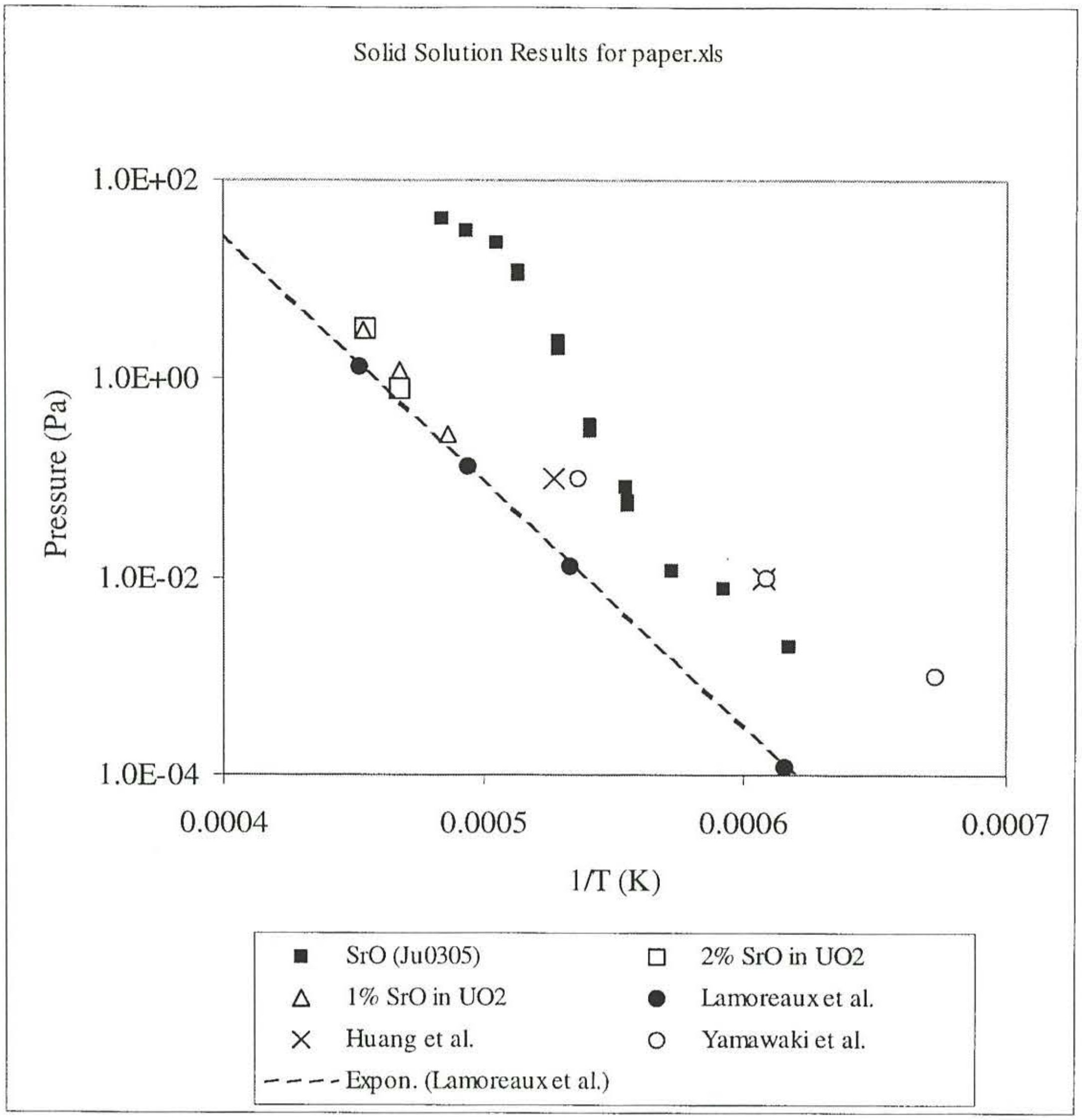

Figure 2: Comparison of Vapour Pressures of Strontium (Sr(g)) Over "Sol-Gel Prepared Solid Solutions" of SrO and UO_2 with those over SrO, reported by Lamoreaux et al.

[11], •; and this work, ■;and and over $SrUO_3$ by Huang et al. [14], ×; and Yamawaski et al. [15], ○. The dashed line is an exponential fit (Clapeyron-Clausius plot) to the data of Lamoreaux et al. for SrO.