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Oxidation of ceramic uranium dioxide in alkali metal carbonate-based melts: a study using various oxidants and comparison with UO_2 powder

Vladimir A. Volkovich [a,1], Trevor R. Griffiths [a,*], Derek J. Fray [b,2], Mark Fields [c,3]

[a] School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom
[b] Department of Mining and Mineral Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom
[c] British Nuclear Fuels plc. (BNFL), R & T North, Sellafield, Seascale, Cumbria CA20 1PG, United Kingdom

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Abstract

The oxidation of broken sintered ceramic UO_2 pellets has been studied between 723 and 1073 K in a range of carbonate-based melts and under a variety of oxidising conditions. Comparison with the oxidation of UO_2 powder under corresponding conditions showed that the reactivity of these media with ceramic UO_2 was less, due to a lower relative surface area and a lower chemical activity of the sintered material. Pure carbonate melts, and with added alkali metal chlorides, produced essentially no reaction with ceramic UO_2. Bubbling the melt with air or oxygen for many hours also had little effect. Addition of nitrate enabled the rate and extent of the reaction to be controlled, by varying the concentration of the oxidising agent and keeping the nitrate-to-UO_2 mole ratio below ~0.4. Above this ratio the available surface area was the main controlling factor of the reaction. Controlled in situ generation of superoxide ions increased significantly the uranate yield at 723 K. A minimum concentration of oxidising agent is thus necessary before reaction commences. Complete oxidation of ceramic UO_2 was achieved in ~2 h at 873 K in carbonate melts that contained KNO_3 and were bubbled with oxygen.

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1. Introduction

The reactions of uranium oxides with molten alkali metal salts of oxo-acids (mainly nitrates or nitrate-based mixtures) have been investigated previously [1–7], the products being various alkali metal uranates. Many uranates have been formed upon heating uranium oxides (UO_2, U_3O_8 or UO_3) with alkali metal carbonates, chlorides, nitrates and peroxides, as well as by reactions in molten salts [8–14]. However, the published data on UO_2 almost entirely refer to reactions of the powder, and reaction of sintered ceramic UO_2 has only been reported in passing by Fujino et al. [1]. They observed that heating pieces of UO_2 pellets with an equimolar amount of $NaNO_3$ in a stream of oxygen for 3 h at 873 K led to complete pulverisation of the pellets with the formation of uranates. They also observed no difference in the reaction on ceramic UO_2 compared with that on the powder under the same conditions. However, in many heterogeneous reactions the reaction rate, for example, will depend mainly on the available surface area. No

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[*] Corresponding author.

[1] On leave from: Department of Rare Metals, Physical-Engineering Faculty, Ural State Technical University-UPI, 19 Mira Ul, 620002, Ekaterinburg, Russia.

[2] Present address: Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK.

[3] Present address: Protea Limited, Magpie Manor, Wistaston Green Road, Crewe CW2 8SA, UK.

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other details were given, and it will be shown that they had more than sufficient oxidants, and time, to effect complete reaction to form $Na_2U_2O_7$.

Oxidation of UO_2 in molten carbonates in the presence of oxygen yields alkali metal uranates as follows:

$$xM_2CO_3 + yUO_2 + y/_2O_2 \rightarrow (M_2O)_x(UO_3)_y + xCO_2 \quad (1)$$

We have found [6] that oxidation of powdered UO_2 in molten carbonates and carbonate-based mixtures proceeds via formation of an insoluble layer of alkali metal uranates on the surface of UO_2 and that the reaction rate is determined by mass transfer of the reactants through this layer. The preparation of the sintered ceramic involves heating the compressed powder in a reducing atmosphere at temperatures well above 1000 K, forming virtually the stoichiometric material, $UO_{2.00}$: urania powder normally contains excess oxygen, taken up in interstitial positions within the fluorite structure. The concentration of oxygen in non-stoichiometric urania is not usually uniform and it is higher on the surface of UO_2 particles. Thus the reactivity of UO_2 powder can be expected to be different from that of the sintered ceramic material.

We had previously found that UO_2 powder was oxidised to a significant extent in fused alkali carbonate mixtures at temperatures as low as 723 K [6], and thus some reaction with ceramic UO_2 was anticipated. In the absence of added oxidising agents the reaction was controlled by the extent of oxygen solubility in the reaction media from the atmosphere above the melt. Increasing the concentration of oxygen species in the melt (e.g., by increasing temperature, oxygen partial pressure or by adding alkali metal chlorides [6,7]) enhanced the melt reactivity towards UO_2 powder. Increasing the oxidising power of the melt by addition of a stronger oxidising agent (e.g., alkali metal nitrate, nitrite, peroxide, superoxide or suitable mixtures thereof) had a marked effect on the reaction. The concentration of the oxidising agent, *i.e.*, alkali nitrate, became the major factor controlling the rate of oxidation of UO_2 powder [5,6]. Finally, controlled generation of superoxide species in the melt (by reaction of alkali metal nitrate with peroxide) has been shown to be the best current method for the oxidation of powdered UO_2 at relatively low temperatures [7]. Since urania powder generally has the formula UO_{2+x} and the ceramic form is normally stoichiometric the claim by Fujino et al. [1] that there was no difference in reactivity seemed to us surprising in the light of the above. Since our studies [6,7] have now provided the conditions for the rapid oxidation of the powder our extensive data would thus provide a sufficient basis for developing a suitable and sensitive method for the complete oxidation of sintered ceramic uranium dioxide in alkali metal carbonate based melts, and a means of testing the statement of Fujino et al. [1].

The results of a study of the oxidation of ceramic UO_2 under a variety of oxidising conditions at temperatures between 723 and 1073 K are reported here.

2. Experimental

The equipment, experimental and analytical techniques have been described previously [6]. The ternary carbonate eutectic (Li_2CO_3:Na_2CO_3:K_2CO_3 = 1.69:1.14:1 mol, melting temperature 666 K) was used in most of the experiments, whilst the binary Na_2CO_3–K_2CO_3 mixture (Na_2CO_3:K_2CO_3 = 1.27:1 mol, melting temperature 983 K) was used at temperatures above 1023 K. All reagents were the purest commercially available. Alkali metal carbonates were dried at 473 K for 4 h prior to use. Sintered ceramic UO_2 pellets, provided by British Nuclear Fuels plc (BNFL), were mechanically crushed into irregular lumps of average size 0.3–2 mm dia (10% of which were smaller particles, down to 0.05 mm dia, as determined by sieve analysis). The average surface area of the mixture of these pieces was 0.2 ± 0.1 m^2 g^{-1} compared with 2.7 ± 0.1 m^2 g^{-1} for UO_2 powder [15]. The ratio of the powder to ceramic surface areas is thus approximately 14 : 1, smaller than might be expected, and attributed to the porosity of the ceramic material (revealed by scanning electron micrographs of our samples of ceramic UO_2). Although the surface of UO_2 particles accessible to gas (for the above measurements) is not the same as that for molten salt, it was assumed that the *ratio* of the surfaces of powder and ceramic forms UO_2 available to the melt would be approximately the same.

Around 1.5 g of UO_2 and 12 g of the eutectic carbonate mixture were used in each experiment. The uranium species formed upon oxidation were characterised by X-ray powder diffraction analysis of quenched melts, using a Phillips PW1710 diffractometer. The concentration of the U(VI) species formed was determined spectrophotometrically [6], using small melt samples (~0.1 g) taken regularly from the crucible. Melt samples were treated with the minimum volume of 1 M H_2SO_4 which dissolves the carbonates present and any uranates formed. Any unreacted UO_2 does not dissolve in dilute sulfuric acid, and since it does not interfere in the subsequent reactions, was not separated off. Uranium(VI) concentration in the solution was determined using the reaction of UO_2^{2+} with Arsenazo I. From over five thousand independent determinations we found the precision of this technique to be under 2%. Any scattering of data resulted mainly from non-uniformity in the composition of heterogeneous melt samples and therefore many determinations were repeated to confirm results and precision.

An alumina crucible was used to contain the molten salt mixtures. The inner surface of the crucible had been pre-treated by reaction with the ternary carbonate melt to form a protective layer of lithium aluminate, $LiAlO_2$, which prevents further reaction of alumina with fused carbonates [16]. Experiments were generally performed in air, and bubbling with oxygen, nitrogen or air was used for stirring the melts. Air was dried (silica gel) and all gases were bubbled through the melt via an alumina tube. Nitrogen was used rather than argon because its density is less than that of air, and hence passing nitrogen through the melt allowed efficient stirring but did not prevent access of air to the melt surface or diminish the oxidising ability of the melt.

3. Results and discussion

3.1. Pure carbonate melts and effect of added chloride

Preliminary experiments showed that an unbroken sintered UO_2 pellet (a rod diameter: 10 mm, length: 12 mm) completely immersed in a stirred $(Na–K)_2CO_3$ melt did not react to produce a uranate, even after 6 h at temperatures up to 1073 K. Under identical conditions samples of UO_2 powder were completely oxidised [6]. Carbonate melts with added alkali metal chlorides have been successfully used for increased oxidation of UO_2 powder [7], because the addition of the chloride leads to increased oxygen solubility in the melt. However, when pieces of broken ceramic UO_2 pellet were reacted in an air-bubbled chloride-containing melt the yield of uranates at 723–823 K was still negligible (<0.5%). The amount of ceramic oxidised however did increase with increasing temperature but even at 1023 K only 6% could be converted to uranates after 7 h. These results suggest that the oxidising species, and their concentration, formed in the melt, due to the reaction of oxygen (from air) with the carbonate, were not sufficient to cause effective oxidation of ceramic UO_2, and a stronger oxidising agent was therefore required.

3.2. Carbonate melt with added nitrate

Alkali metal nitrates have been shown to be very effective [6] for the oxidation of UO_2 powder: a $KNO_3 : UO_2$ mole ratio of around 0.4 was sufficient for complete oxidation at 723 K in ~1 h. Fig. 1(A) shows the results of the reaction of ceramic and UO_2 powder in the ternary carbonate melt with varying amounts of KNO_3 added. The extent of reaction is presented as changes in uranium-to-oxygen atomic ratio, equal to 2 for UO_2 and to 3 for an alkali metal uranate of general formula $(M_2O)_x(UO_3)_y$. This ratio is shown as a function of time at various initial concentrations of oxidising agent and, as expected, the oxidation of the ceramic material proceeded more slowly: on a weight-for-weight basis the ceramic material was oxidised around 100 times more slowly than the powder. The yield of the uranate species increased linearly with time over a 13 h period, though the results are only shown for the first 7 h. This figure reveals clearly the different behaviour between these two forms of UO_2 from that previously reported [1]. Further, the results with UO_2 powder showed an initial rapid increase in the concentration of uranates, with essentially no further oxidation of UO_2 after 1–2 h. Also, the oxidation of powder and ceramic UO_2 differed in that the extent of the reaction of ceramic UO_2 depends upon the concentration of KNO_3, but only up to a limiting mole ratio of $KNO_3 : UO_2$ of ~0.4, Fig. 1(B). Beyond this ratio the surface area of UO_2 (and not the concentration of the oxidising species) determines the extent and the rate of the reaction. A minimum concentration of these oxidising agents is thus required before ceramic UO_2 can be oxidised.

3.3. Mechanism of the oxidation of ceramic UO_2

X-ray powder diffraction analysis showed that potassium diuranate was the main product formed upon oxidation of ceramic UO_2 in carbonate melts with added KNO_3, in agreement with our work on the oxidation of UO_2 powder [6]. The mechanism by which oxidation of the ceramic form of UO_2 proceeded must, however, be somewhat different. With UO_2 powder a solid layer of uranates is gradually built up on the surface of the particles, causing the reaction essentially to cease after 2–4 h [6]. Examination of the large particles of the ceramic showed no evidence of such a layer. Instead, the insoluble uranate species formed initially on the surface did not adhere and were released into the melt. We suggest that the intrusion of oxygen atoms into the UO_2 structure upon oxidation leads to the initial formation of species such as U_4O_9 and U_3O_8 uranium oxides and that these cause considerable expansion in the volume of the surface layer, and subsequent fracture of the layer of uranates formed on the surface of the particle can be expected. For small ceramic particles and UO_2 powder this expansion is insufficient to dislodge uranate particles, but will do so by spalling in the course of oxidation of larger pieces of ceramic UO_2. Thus this spalling and oxidation of lumps of ceramic UO_2 pellet leads to pulverisation of the material and the formation of uranates, in agreement with the observations of Fujino et al. [1] using pure molten $NaNO_3$.

3.4. Effect of agitation of nitrate-containing melts

Upon bubbling oxygen through the ternary carbonate eutectic melt containing KNO_3 further increase in the oxidation of the ceramic was observed, but even after 7 h at 723 K the reaction was still far from complete. Fig. 2 shows the effect of temperature upon the

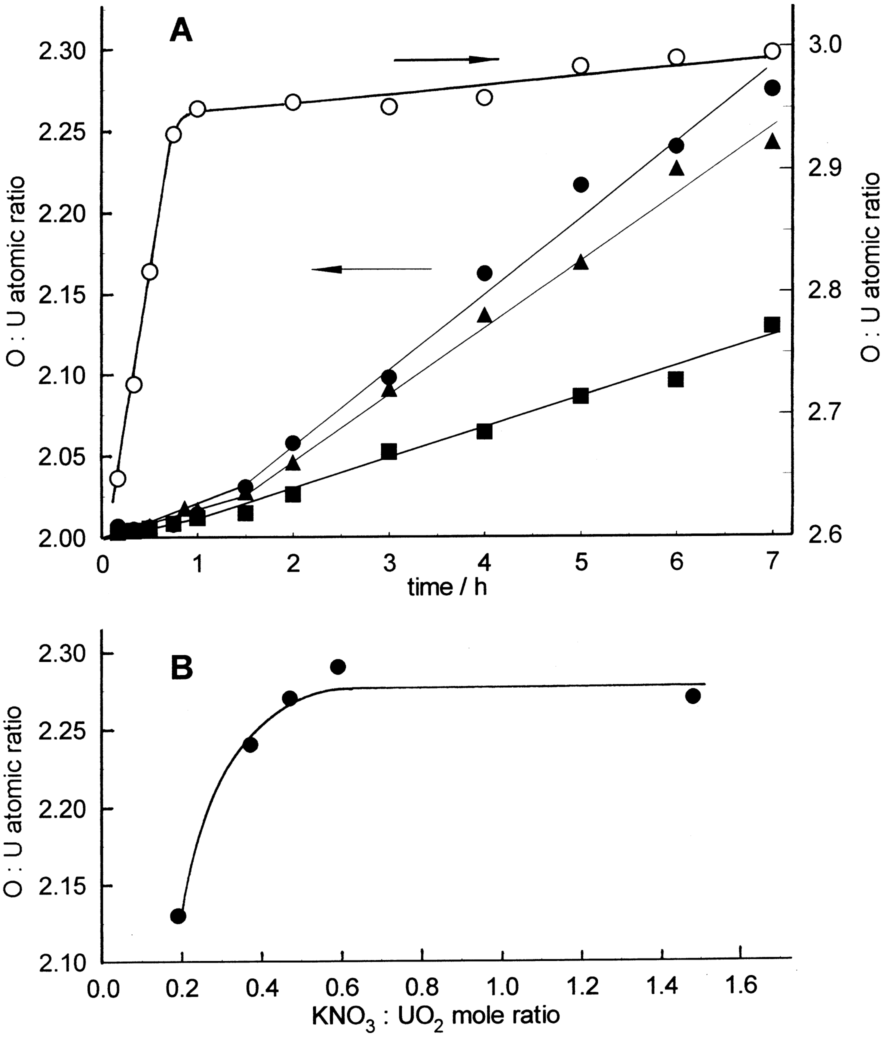

Fig. 1. Effect of KNO_3 concentration on oxidation of UO_2 at 723 K in the ternary eutectic, $(Li–Na–K)_2CO_3$. (A) Over time, solid symbols – ceramic UO_2, empty symbols – UO_2 powder. Molar ratio of $KNO_3 : UO_2$ of: (■), 0.19; (▲), 0.37; (●), 0.59 and (○), 0.41. (B) Extent of the oxidation of the ceramic after 7 h at various $KNO_3 : UO_2$ mole ratios.

oxidation of ceramic UO_2 in a melt bubbled with oxygen and having a mole ratio of $KNO_3 : UO_2$ of ca. 0.4. These plots are again different from those previously obtained for the oxidation of UO_2 powder [6]. At 723 K ceramic UO_2 oxidised slowly and steadily over 7 h, but at 773 K it oxidised slowly at first, the rate increasing after around 1 h, and subsequently slowing after the third hour. The reaction observed here follows that found for the powder at 823 and 873 K, with subsequent slowing of the rate after 2 h at both temperatures. The reaction virtually ceased at 873 K after 2 h. The yield of uranates obtained after 7 h was between 96% and 98%. Thus it was possible to determine the minimum conditions to achieve complete oxidation of ceramic UO_2. In these melts, bubbled with oxygen, a significantly smaller nitrate-to-UO_2 ratio (0.4) was required than that of 1.0 implied by Fujino et al. [1] in their single condition experiments using the more oxidising pure $NaNO_3$ melt under an oxygen atmosphere. Further, we found that complete oxidation of ceramic UO_2, at 873 K, was obtained in 2 h (Fig. 2), whereas they reported uranate formation in 3 h at the same temperature (but without apparently testing with shorter time intervals).

There are two possible mechanisms by which bubbling oxygen through nitrate-containing melts that affect UO_2 oxidation. First, bubbling oxygen or, indeed any gas, through the melt provides agitation and thus facilitates contact between molten salt and heavy urania particles (normally concentrated on the bottom of the crucible), and we have shown previously that simple mechanical

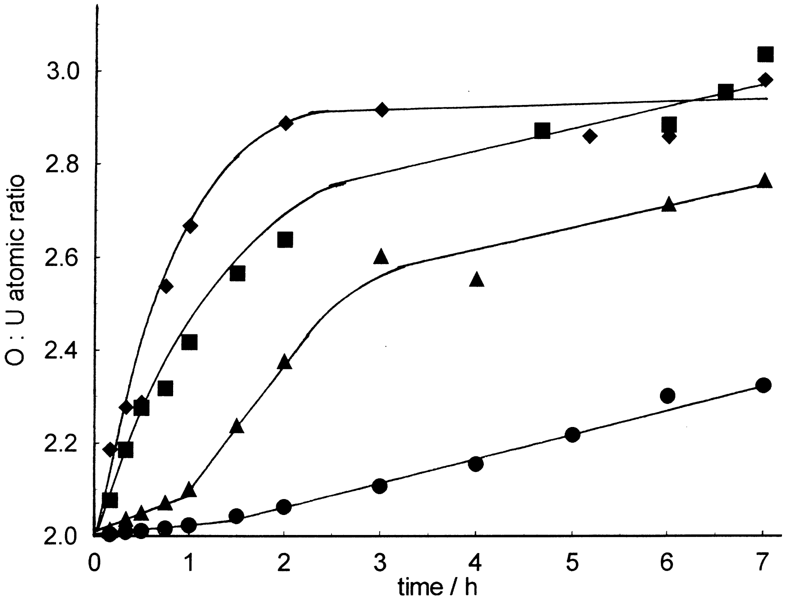

Fig. 2. Effect of temperature on oxidation of ceramic UO_2 in $(Li–Na–K)_2CO_3–KNO_3$ melts bubbled with oxygen at a flow rate of 2.7 dm^{-3} h^{-1} and mole ratio of KNO_3 : UO_2 of 0.46.(●), 723 K; (▲), 773 K; (■), 823 K and (◆), 873 K.

stirring of the melt enhanced oxidation of UO_2 powder [6]. Second, bubbling oxygen increases the amount of oxygen chemically dissolved and hence increases the concentration of peroxide or superoxide species [17–22]:

$$2CO_3^{2-} + O_2 \Longleftrightarrow 2O_2^{2-} + 2CO_2 \qquad (2)$$

$$2CO_3^{2-} + 3O_2 \Longleftrightarrow 4O_2^{-} + 2CO_2. \qquad (3)$$

This arises because oxygen only undergoes chemical dissolution in molten carbonates and its solubility increases with temperature increase [23]. A series of experiments on ceramic UO_2 performed at 773 and 823 K showed that bubbling air through a carbonate melt containing added nitrate gave the same effect as bubbling oxygen and the fraction of the ceramic oxidised in these melts bubbled with nitrogen was the same as that achieved under static conditions. Thus simple agitation of the melt with nitrogen gas did not facilitate the oxidation of ceramic UO_2, and the increase in the yield of uranates in oxygen-bubbled melts was due to the increased concentration of peroxide/superoxide species in the melt. We further suggest that the observed lack of difference in the extent of oxidation in air- and oxygen-bubbled melts arises because changes in the relative concentrations of peroxide/superoxide ions in the melt had essentially no effect on oxidation of ceramic UO_2. This is contrary to our findings for the oxidation of UO_2 powder [6], where increasing the partial pressure of oxygen facilitated superoxide formation, due to shifting the peroxide-superoxide equilibrium to the right:

$$O_2^{2-} + O_2 \Longleftrightarrow 2O_2^{-} \qquad (4)$$

and therefore enhances UO_2 oxidation. Reactions (5) and (6) show that superoxide oxidises 1.5 times more UO_2 than peroxide:

$$O_2^{2-} + UO_2 \rightarrow UO_3 + O^{2-} \qquad (5)$$

$$2O_2^{-} + 3UO_2 \rightarrow 3UO_3 + O^{2-}. \qquad (6)$$

3.5. *Chemical generation of superoxide ions in situ*

In our previous study of the oxidation of UO_2 powder, carbonate melts with added alkali metal nitrate and peroxide were shown to be most effective [7]. We found that the reaction of peroxide that occurs in molten nitrates [24] applies in molten carbonates:

$$2MNO_3 + M_2O_2 \rightarrow 2MNO_2 + 2MO_2. \qquad (7)$$

Around three times excess of the peroxide above the stoichiometry of reaction (7) was necessary to produce a considerable concentration of superoxide ions in the $(Li–Na–K)_2CO_3–KNO_3–Na_2O_2$ melt containing UO_2 powder. Fig. 3 shows that addition of Na_2O_2 to the ternary eutectic melt had very little effect on the oxidation of ceramic UO_2 at 723 K. However, when the peroxide was added into the same melt together with KNO_3, reaction occurred. The total uranate yield significantly increased compared with that expected from simple

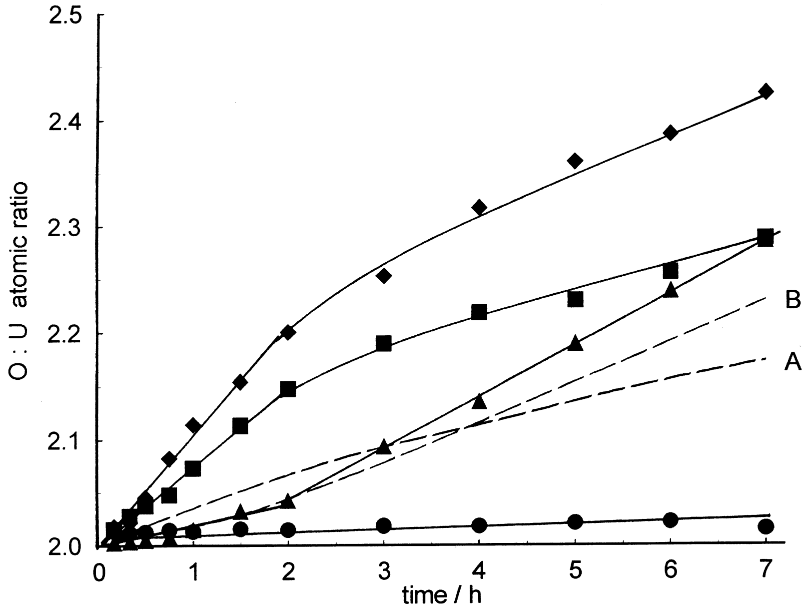

Fig. 3. Oxidation of ceramic UO_2 in the ternary carbonate eutectic with added KNO_3 and Na_2O_2 at 723 K. Solid lines represent experimental data and dashed lines the expected extent of the reaction due to simple additive influence from KNO_3 and Na_2O_2. Mole ratios of KNO_3 : UO_2 and Na_2O_2 : UO_2 of: (●), 0 and 0.97; (▲), 0.59 and 0; (■), 0.25 and 1.00 (A); (♦), 0.46 and 0.36 (B), respectively.

additive mixing of Na_2O_2 and KNO_3. Dashed lines in Fig. 3 represent this expected yield for various melt compositions. It was possible to increase the degree of UO_2 oxidation by ca. 80% by keeping the KNO_3 : UO_2 mole ratio low, around 0.5, (which produced the maximum effect, Fig. 1(B)), and by adding a small amount of sodium peroxide. Raising the peroxide-to-nitrate mole ratio led to a slight decrease in the efficiency of the system: at a ratio of 4 the increase in UO_2 oxidation was only ca. 60%. We therefore conclude that the optimal conditions for reaction (7) in the system containing ceramic UO_2 require a considerably smaller peroxide-to-nitrate mole ratio compared with that required for oxidation of the powder, viz., 0.8 compared with 3. This is closer to the ratio of 0.5 required by the stoichiometry of reaction (7) and hence is in agreement with our above finding that the reactivity of Na_2O_2 with ceramic UO_2 is low (Fig. 3). Added peroxide tends to react only with the nitrate present. This reaction differs from that in melts containing UO_2 powder, where some of the peroxide is consumed by reaction with UO_2 (Eq. (5)). Apart from increasing the amount of UO_2 oxidised, addition of Na_2O_2 to the melt containing KNO_3 significantly improved the rate of oxidation of ceramic UO_2, especially in the initial 2–3 h, after which the reaction slowed down (Fig. 3). It is thus possible to generate in situ a significant amount of active superoxide species in carbonate melts so that the extent and rate of oxidation of ceramic UO_2 are both increased while maintaining relatively low temperatures.

3.6. Attempts to increase further the performance of the system

There are two general approaches for increasing oxidation of UO_2 in carbonate melts. First, the concentration of oxidising species in the melt is increased by passing air/oxygen through the melt or by increasing the oxygen partial pressure in the atmosphere above the melt. Second, increasing temperature enhances the reactivity of these media towards UO_2 and also increases oxygen solubility.

As noted above, the oxidation of ceramic UO_2 in KNO_3-containing carbonate melts was increased by bubbling air/oxygen through the melt. However, bubbling air or oxygen through a carbonate melt containing two oxidising agents, nitrate and peroxide, did not improve the oxidative capability of the system towards ceramic UO_2. The yield of uranates was essentially the same as that achieved under static conditions with the same amount of added oxidising agents. This was initially surprising since air/oxygen bubbling increases the formation of oxygen species in the melt, viz., peroxide or superoxide (reactions (2–4)). However, the concentration of peroxide or superoxide ions in the melts containing both nitrate and peroxide is significantly higher than that formed as a result of oxygen dissolution. Oxygen solubility in molten carbonates is of the order of 10^{-4} mole dm^{-3} atm^{-1} [23] and as a result the peroxide/superoxide species formed in our experiments here could not increase significantly the oxidative power of the melt.

Increasing the temperature had a negative effect on reaction (7) due to the thermal decomposition of the added peroxide and therefore the concentration of superoxide ions decreased. At 823 K the extent of UO_2 oxidation in air-bubbled nitrate and nitrate-peroxide containing carbonate melts was the same. Hence it was not possible to achieve complete oxidation of ceramic UO_2 using this system, a system shown to be highly effective for oxidation of UO_2 powder [7].

3.7. Reactivity of ceramic UO_2

The above findings clearly show that the reactivity of ceramic uranium dioxide is significantly less than that of the powder, contrary to the assertion of Fujino et al. [1], who declared that “no significant difference was observed in the reaction [with $NaNO_3$] where sintered UO_2 pellet was used instead of powder”. Further, it is important to note that our ceramic material was essentially unattacked by all our pure, air-bubbled, carbonate melts up to the maximum temperature used of 1073 K. In identical melts UO_2 powder was significantly oxidised at the lower temperatue of 723 K and could be completely converted into uranates at 1023 K [6]. In carbonate melts containing added chloride, ceramic UO_2 was only slightly oxidised at 1023 K after 7 h immersion and agitation by air-bubbling, while under the same conditions 10 wt% of the powder form of UO_2 could be oxidised completely at 823 K [7].

Comparison of the results presented in Fig. 1(A) shows that ceramic UO_2 was oxidised 120 ± 20 times slower than the same amount of powder in the first 30 min after commencing the reaction (after which time all the UO_2 powder added had been oxidised completely). This ratio is almost 10 times greater than the ratio of available surface areas of powder and ceramic materials. Further, complete oxidation of a mixture of 10 wt% of UO_2 in the ternary carbonate melt containing KNO_3 (723 K, $KNO_3 : UO_2$ mole ratio of 0.4) took around 30 min for the powder to be oxidised whereas less than half the ceramic material was oxidised in 13 h. The available surface area of the ceramic in this case was only 13.5 times less than that of the powder and therefore complete oxidation of the ceramic could be expected in ~7 h if its reactivity was equal to that of the powder.

To account for this difference in the reactivity of ceramic UO_2 in carbonate-based melts with that of the powder we first address the surface differences between uranium dioxide in powder and ceramic forms. The powder reacts slowly with oxygen in air at room temperature. Our own sample changed its value of x, in UO_{2+x}, from 0.08 to 0.10 a year later, a difference considerably greater than our analytical precision. Stoichiometric single crystal UO_2 undergoes surface oxidation at ambient temperatures much more slowly. One of us has been involved in the determination of the chemical-diffusion coefficient of oxygen in single crystal UO_{2+x} over the range 453–573 K [25]. We have extrapolated these linear data to 293 K and obtained the very low surface oxidation diffusion value of 10^{-21} cm^2 s^{-1}. In the preparation of ceramic UO_2 the powder is first mixed with a trace of organic binder, then compressed cold and finally heated under hydrogen at 1300–2100 K for around 24 h. The binder is thus driven of and the UO_{2+x} reduced to stoichiometric, or slightly sub-stoichiometric urania. Importantly, the ceramic pellets formed are not exposed to air until they have cooled to ambient temperatures. Our ceramic samples have not changed their formulation in a 12-month period. UO_2 powder therefore reacts more rapidly because its surface and bulk contain interstitial oxygen, which the ceramic form essentially does not. The ceramic form, as we have shown here, has to have a minimum concentration of oxidising species in the carbonate medium before it starts to react to form uranate, and the concentration maintained by simple oxygen dissolution is not sufficient to initiate oxidation. In addition, there may be an induction time, before which oxide ions penetrate the ceramic surface, that is dependent upon both temperature and the concentration of the oxidising species. For example, Fig. 2 indicates an induction period of just over 1 h at 723 K and just under at 773 K. A similar feature may be seen in Fig. 1.

An interesting experiment would be to examine the surface of samples of ceramic UO_{2+x} after increasing intervals of exposure to oxidation in molten carbonate. It will then be possible to establish if, when the surface stoichiometry has become that of the powder, the oxidation rates will be the same. At this time we do not have the facilities to undertake such investigation.

4. Conclusions

The oxidation of ceramic uranium dioxide is different from that of the powder, contrary to an earlier conclusion [1], can be achieved in alkali metal carbonate-based melts, and leads to the formation of alkali metal uranate(VI) species. The reactivity of pure ternary carbonate with ceramic UO_2 was barely detectable and that of carbonate–chloride mixtures with the ceramic was found to be very low: at 1023 K only 6% of the ceramic was oxidised after 7 h. Addition of potassium nitrate enabled complete oxidation of ceramic UO_2 samples in 2 h at 873 K in an oxygen bubbled ternary carbonate melt, and potassium diuranate was the main product. Replacing oxygen with air did not alter the rate and extent of oxidation of ceramic UO_2 within experimental error. The ceramic form of UO_2 is less sensitive towards the concentration of oxygen species formed upon the dissolution of oxygen in the melt, contrary to the findings reported earlier with UO_2 powder [6]. A minimum concentration of the oxidising species peroxide/superoxide is necessary before stoichiometric ceramic UO_2 can be oxidised in carbonate melts. Controlled, in situ, generation of superoxide species in the ternary carbonate melt was achieved by the reaction of KNO_3 with Na_2O_2 and oxidation of ceramic UO_2 then occurred at 723 K. However, increasing the temperature to 773 K and above did not further increase the oxidation of the ceramic, due to thermal decomposition of the peroxide. The reactivity of ceramic UO_2 in these melts was nearly an order of magnitude slower than that of the powder when the surface areas were ratioed. This difference is attributed to the difference in stoichiometry between the ceramic and powder forms of uranium dioxide, which affects the response and reactivity of UO_2 to oxidising agents.

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