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Production and use of radioactive [⁸²Br]KBr in high-temperature corrosion studies



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ABSTRACT

The applicability of radioactive species in high-temperature research as tracers was studied with KBr and an Nbstabilised austenitic stainless steel. KBr-induced high-temperature corrosion was addressed by using radioactive [82Br]KBr and measuring the radioactivity of the sample surface with a high-resolution phosphor imaging device.

Neutron activation by cyclotron proved to be a very cost-effective way to produce radioactive [82Br]KBr with a high radionuclidic purity and a negligible level of unwanted side products. KBr reacts rapidly with steel, forming potassium chromate and metal bromides, both of which are reducing the protective properties of the surface oxide through chromium depletion and increasing porosity.

1. Introduction

The growing need for electricity and interest in replacing fossil fuels with renewable ones have together drawn attention to a diverse pool of potential fuels. Traditionally, biomass such as forest residues and straws have been used due to their availability, CO2-neutrality, and governmental legislation. These fuels typically contain considerable amounts of Ca, K, Na, Cl, and S, which are held responsible for high-temperature corrosion and fly ash melting, resulting in decreased efficiency and increased operational costs through maintenance operations [1-3]. More recently, new alternatives for renewable fuels have emerged to the side of the abovementioned nature-based fuels. These include, among others, solid recovered fuels (SRFs), which are very heterogeneous from their chemical composition, containing Pb, Zn, and Br, for example [4-6]. The presence of these elements generates a new kind of high-temperature chemistry in the form of reactions occurring in the gas phase and in the deposits forming on the heat-transfer surfaces. Therefore, studies on the reactivity of Br-containing species such as potassium bromide (KBr), have become more relevant in terms of industrial applications.

So far, the knowledge of potassium bromide-induced corrosion has been scarce, mainly due to the low concentration of KBr in combusted solid fuels. Nowadays, bromine is constantly used as brominated flame retardants (BFRs) in electronic equipment, textiles, and insulation foams, which has increased the concentrations of bromine-containing species in waste combustion [7]. This has initiated studies on the corrosivity of metal [8] and alkali [9,10] bromides at temperatures relevant to waste combustion. In the case of KBr, it was found corrosive towards various commercial heat-transfer alloys in the tested temperature range of 400–600 °C [9,10]. The severity of corrosion depended on alloy quality, prevailed temperature and atmosphere. It was proposed that the protective chromia (Cr_2O_3) at the alloy surface is destroyed through potassium chromate (K_2CrO_4) formation, resulting in Cr-depletion of the surface oxide, making it more prone to further material degradation (Eqs. 1a,b). However, the potassium chromate was not definitely identified, in addition to which some initial reaction stages might have left unnoticed due to the long exposure time. Therefore, the first goal of this study is to focus on the initiation of the KBr-induced high-temperature corrosion and to shed more light on the reaction mechanism.

$$8KBr(s) + 2Cr_2O_3(s) + 5O_2(g) \to 4K_2CrO_4(s) + 4Br_2(g)$$
(1a)

 $8KBr(s) + 2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \rightarrow 4K_2CrO_4(s) + 8HBr(g)$ (11)

(1b)

Radioactive species have long been used as tracer elements in medical studies [e.g. 11-13] or in studies addressing industrial applications under atmospheric conditions [14–16], but their utilization in high-temperature research has been less common. So far, radioactive species have been used to study, for example, petrochemical and refinery processes (¹⁰⁸Ag) [17], diffusion (²⁶Al) [18] (⁶³Ni) [19], or

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surface adsorption (¹³⁴Cs) [20]. In industrial applications, the use of radioactive [⁸²Br]KBr has been focusing on studies addressing flow patterns [21], leakage localization [22], or wastewater dilution [23], but very little information on the possibility to use [⁸²Br]KBr to study high-temperature phenomena such as diffusion or corrosion has been published.

Until now, radioactive species have been synthesized by neutron or gamma irradiation in nuclear reactors [e.g. 24,25], making their availability in research laboratories difficult. The production of the ⁸²Br is typically based on a thermal neutron-induced (n, γ) reaction, where neutrons of a large energy spectrum originate from a nuclear reactor core [24,26,27]. Required neutron fluxes are typically high, as is the exposure time (tens of hours), in order to obtain desired amounts (activity) of the isotope in the form of KBr. This method further relies on allowing short-lived isotopes, which are also produced, to decay in order to achieve the radionuclidically pure [⁸²Br]KBr.

In order to widen the possibilities to utilize radioactive tracers in high-temperature studies, a more cost-efficient synthesis route should be discovered. The second goal of this study is to investigate the possibility to produce radioactive [⁸²Br] labeled KBr by neutron activation at a cyclotron and to evaluate the applicability of [⁸²Br]KBr in high-temperature studies.

2. Materials and methods

The radioactive [⁸²Br]KBr was produced by bombarding suprapur KBr with neutrons, obtained as a secondary product during proton irradiation of ¹⁸O-enriched water in an Advanced Cyclotron Systems Inc. TR-19 cyclotron. Radioactive fluorine, [¹⁸F]F₂, is regularly produced at the Turku PET Centre utilizing the nuclear reaction of ¹⁸O(p,n)¹⁸F. The neutrons produced in the reaction are normally considered a nuisance as they induce unwanted radioactivity in the surrounding constructions. The target station, where the radioactive fluorine is produced, is therefore often located inside a neutron shield containing mostly water to absorb the neutrons. In this case, however, the neutrons were used to produce ⁸²Br.

The ⁸²Br was produced by the nuclear reaction ⁸¹Br(n,g)⁸²Br. Small amounts of KBr (250 mg, Sigma Aldrich, ACS grade) in 1.5 ml Eppendorf (Protein Low-bind tube) vials were placed in a paraffin block inside the neutron shield about 20 cm behind the fluorine target at the cyclotron. As the reaction cross section is highest at the neutron energy of 0.1 keV (13 b) and the neutrons from the ¹⁸O(p,n)¹⁸F reaction have an energy distribution with a maximum around 2 MeV, a paraffin block with a wall thickness of 50 mm was used to decrease the neutron energy and thereby optimize the production of ⁸²Br. The used wall thickness of 50 mm has been found in separate tests to sufficiently reduce the energy of neutrons originating from the ¹⁸O(p,n)¹⁸F reaction and thereby increase the probability for neutron capture in ⁸¹Br.

It was found that a one-hour irradiation of ¹⁸O-enriched water with 18 MeV protons at a beam current of 100 μ A yielded a total activity (at EOB) of 200 GBq of ¹⁸F and an activity concentration of 54 kBq g⁻¹ ⁸²Br in the KBr salt. The neutron flux from the *p*,n reaction was in the order of 10¹² neutrons per second at this current. After the end of bombardment, the samples were allowed to decay for about 12 h before they were removed from the neutron shield. The production of ⁸⁰Br from the other stable isotope of bromine (⁷⁹Br(*n*,*g*)⁸⁰Br) was not a problem due to the short half-life (T_{1/2} = 17.68 min). No gamma rays were observed from potassium.

There are several advantages with this approach; there is no need for separation chemistry as the radioactive bromine is perfectly mixed with inactive potassium bromine. It seems to be perfectly free from radioactive contaminants and no additional expensive irradiation is needed as it is produced simultaneously as the radioactive ¹⁸F is produced for PET studies. In addition, the low activity and short half-life (35.3 h) of ⁸²Br make the produced [⁸²Br]KBr comparatively safe to use.

After removal from the neutron shield, [82Br]KBr was pressed

Table 1 The nominal chemical composition of the studied allov in wt%

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Steel	Cr	Fe	Mn	Мо	Ni	Si	Others
AISI347	17.7	68.2	2.1	-	8.5	0.4	Nb 1.5

(200 bar, 15 s) into flat cylindrical pellets with an average mass of 530 mg, a standard diameter of 8 mm, and a thickness of 2 mm.

An Ortec coaxial HPGe semiconductor detector was used to assess the radioactivity of the pellet. An acquisition time of 10 min was used with the pellet on a distance of 10 cm from the end cup of the detector. An additional measurement was performed a week after the activation to verify the radionuclidic purity of the pellet. The obtained spectrum was analyzed with the FitzPeaks Gamma Analysis software (version 4.01, 10th April 2008). The quality was checked using certified calibrated point sources of ¹³⁷Cs, ⁶⁰Co and an uncalibrated source of ¹⁵²Eu.

The steel samples were cut from a Nb-stabilized austenitic stainless steel superheater tube into quadratic pieces of the size $(20 \cdot 20 \cdot 10)$ mm³ (Table 1). To remove the scratches and to create a reproducible surface roughness, the sample pieces were polished first with water and a Grit 280/P320-SiC paper, then with water and a Grit 500/P1000-SiC paper and finally, cleansed in an ultrasonic bath with ethanol. Before the exposure, the [⁸²Br]KBr pellet was placed in the corner of the steel surface and kept in position with a weight (Fig. 1). The exposures were carried out in a temperature-controlled tube furnace, where the sample was located in a quartz reactor. The furnace was heated up to 550 °C with a heating rate of 5 $^{\circ}$ C min⁻¹ and kept at the target temperature in flowing synthetic air $(0.15 \text{ dm}^3 \text{ min}^{-1})$ for 2, 5, 8, 12, and 24 h. After the exposure, the furnace was shut off and let cool down to room temperature. The reactor was purged with nitrogen both during the heating and cooling to avoid the initiation or continuation of possible oxygen-involving reactions.

After the predetermined exposure time (2, 5, 8, 12, and 24 h), the [82 Br]KBr pellet was removed from the steel surface, which was first analyzed with a high-resolution (25 µm) phosphor imaging device (Fujifilm FLA-5100 with an Eu-doped BaBrF screen). Due to the low initial activity concentration of the salt and the comparatively long half-life, the phosphor screen exposure time was chosen as 24 h in order to provide sufficient activity resolution in the image before the image was scanned with the FLA-5100 reader. As phosphor screen, a BAS-TR2025 with a size of 20 x 25 cm (Fuji Photo Film CO LTD, Japan) was used.

The images were calibrated by spreading a small amount of [⁸²Br] KBr (97 mg, 747 Bq) over a piece of adhesive tape which was wrapped into a plastic bag and placed into an exposure cassette with the phosphor screen. After an exposure of 24 h, the screen was scanned using the FLA-5100 reader. The data were analyzed using the Tina 2.0 software (Raytest Isotopenmessgeräte GmbH, Straubenhardt, Germany). The number of counts was obtained by integrating over the area on the image that corresponded to the area on the tape where the radioactive salt had been spread. The background was subtracted from the counts. The ratio between the activity and the number of counts as well as the ratio between the activity and the amount of KBr could now be applied to determine the amount of Br on the steel surface.

After each activity measurements, the sample surface was studied using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) with a focus on surface morphologies and chemical compositions of local structures. The microscope (SEM-LEO Gemini 1530 with a NORAN Vantage X-ray analyzing system manufactured by Thermo Fisher Scientific) was operated in secondary and backscattering electron modes at an accelerating voltage of 15 kV for the EDX analyses and for imaging with an aperture size of $60 \,\mu\text{m}$ and a beam current of 1 nA. SEM micrographs were recorded with 30- to 25,000-fold magnifications.



Fig. 1. A schematic of the experimental setup.



Fig. 2. Spectrum of [⁸²Br]KBr pellet recorded with an HPGe detector a week after the end of bombardment (EOB). The distance to the detector was 10 cm and the acquisition time was 6372 s. The peak at 1460 keV (⁴⁰K) is part of the normal radiation background.

3. Results and discussion

3.1. Production of [82Br]KBr

The radionuclidic purity of the produced [^{82}Br]KBr was very high; no traces of 42 K or 80 Br could be observed at any time (Fig. 2). The 40 K peak in the spectrum is from the natural radiation background. At the beginning of every exposure of the steel in the tube furnace, the average activity of [82 Br]KBr was 18.9 kBq (in a 500 mg pellet), measured after the exposure and calculated back to the start time of the exposure.

Before studying the exposed steel surfaces, the sensitivity and resolution of the phosphor imaging device were addressed by exposing it to a produced [82Br]KBr pellet for two minutes (Fig. 3). Both the radioactivity and its intensity variations are clearly visible in the image, demonstrating the possibility to use [82Br]KBr in high-temperature studies. After the promising result with the sole [⁸²Br]KBr pellet, the steel surfaces reacted with the salt were imaged after the exposures (Fig. 4). The original location of the pellet is clearly visible, even after the longest exposure time of 24 h. The separate bright spots best visible at surfaces exposed for 2, 8, and 24 h originate from the thermal cracking of the pellet, resulting in the rejection of small pieces of the pellet. The diameters of the radioactive regions in the films did not increase significantly as a function of time, indicating that the lateral diffusion of [82Br]KBr along the steel surface is slow, at least in the beginning of the reaction. This corresponds well with the total amounts of Br on the steel surface. The amounts of Br on the steel surfaces were calculated as 42 ng (2 h), 37 ng (5 h), 361 ng (8 h), 71 ng (12 h), and 35 (24 h), taking into account the radioactive decay. The high amount of Br on the surface after the eight-hour exposure in 550 °C can only be explained by material from the pellet adhering directly to the sample



Fig. 3. The radiation intensity of a manufactured [⁸²Br]KBr pellet, measured in a two minutes-exposure on a phosphor screen. The redder the color, the higher the radioactivity.

surface. It should also be noted that a remarkably high amount of Br was detected on the surface of the sample exposed for 12 h. This will be discussed in detail later in the text.

The very high sensitivity of the phosphorous film, combined with the location specificity of the activity distribution and with the possibility to detect radioactivity even after a 24-hour exposure, further supports the applicability of $[^{82}Br]KBr$ in studies addressing the initial stages of high-temperature phenomena such as corrosion or diffusion.

Taking into account the low amounts of activity required in the corrosion tests, we propose that the method presented in this paper is a valuable addition to the more conventional ⁸²Br production methods, especially as the [⁸²Br]KBr is conveniently obtained as a "side product" during normal ¹⁸F-production for radiotracer synthesis and subsequent PET (positron emission tomography)-use.

3.2. [82Br]KBr -induced high-temperature corrosion

The reaction between KBr and the steel surface initiated shortly after the introduction of air: small pores, clusters, and separate particles formed within 120 min (Fig. 5). The steel surface without any fine structure consisted of an oxide containing iron and chromium in the same ratio as in the bulk material. The formed oxide was most likely so thin that the depth resolution of the scanning electron microscope was not high enough to analyze the sole oxide, but collected information also from the material beneath the formed oxide. However, at a slightly lower temperature of 500 °C, a 22 nm thick oxide containing iron and chromium formed in a 5-hour exposure [28]. It is very likely that an oxide with a similar composition formed also in the present study. In addition to chromium, the separate particles formed onto the steel surface contained potassium up to 9.5 at.% with only traces of bromine. This indicates the formation of potassium chromate (K₂CrO₄) according



Fig. 4. The activity maps of the phosphor screens exposed to the AISI 347 steel surfaces reacted with [82Br]KBr at 550 °C for; a) 2 h, b) 5 h, c) 8 h, d) 12 h, e) 24 h.



Fig. 5. The AISI 347 steel surface with pores and K_2CrO_4 particles (dark grey) after being exposed to $[^{82}Br]KBr$ at 550 °C for 2 h.

to the principle presented in Equation 1. However, the presence of pores piercing the steel surface implies that gaseous species other than Br_2 could have been involved in the reaction. The formation of K_2CrO_4 has been verified in the reaction between KCl and the protective chromium oxide (Cr_2O_3) already after very short time [29]. Such a rapid reaction has not been previously reported in the case with KBr, but the immediate formation of K_2CrO_4 with both potassium halides points out the active role of potassium in the initiation of the high-temperature corrosion reaction.

The separate clusters formed at the surface contained oxygen, chromium, iron, and niobium with niobium concentrations close to 8 at.%, which substantially exceeds the bulk concentration of niobium (Fig. 6). Similar Nb-rich nodules formed on the AISI 347 steel also in the absence of any solid salt at 500 °C [28], suggesting that the oxidation of niobium acts as an initial step in the local degradation of the surface oxide, resulting in the formation of non-protective clusters. The detected niobium oxide is most likely niobium pentoxide (Nb₂O₅), which forms rapidly at temperatures below 600 °C [30]. The formation of

Nb₂O₅ is associated with significant stresses, leading to the plastic deformation of the steel and the oxide and finally, to the appearing of cracks. Such cracks provide fast diffusion pathways for oxygen and corrosive species to penetrate the surface oxide and to react with other elements in the bulk material. In the case of Nb-Ti-Al alloys, the addition of chromium is reported to increase the heat resistance of the alloys due to the formation of a protective chromium oxide and due to the presence of NbCr₂, which prevents Nb to diffuse towards the surface layer, where it oxidizes [31]. Apparently, such beneficial effect of chromium on uncontrolled Nb-oxidation cannot be achieved in Fe-Cr-Nb alloys. The presence of small pores supports further the hypothesis of gas transport through the surface oxide (Fig. 7). Interestingly, the rims of the pores contained niobium up to 6.5 at.%, suggesting that Nb would also play a role, one way or the other, in the pore formation. In the case of solid chlorides, metal chlorides tend to form at the steel/ oxide interface, where the oxygen partial pressure is low enough to keep metal chlorides stable [32]. As soon as the metal chlorides diffuse towards the surface and thus, towards higher oxygen partial pressure, they rapidly oxidize. The pores formed in the presence of KBr suggest that a similar reaction might have occurred. However, due to the small size of the pores, no indication of metal bromide formation was obtained.

The number of pores, clusters, and K_2CrO_4 particles had increased during the five-hour exposure (Fig. 8). In addition to the increased number of K_2CrO_4 particles, they appeared thicker and larger in size, most likely through coalescing of individual particles into larger entities. Whether the coalescence can be attributed to surface diffusion of K_2CrO_4 or to the formation of new K_2CrO_4 particles as a function of time, remained elusive at this point of the research. It is also visible in Fig. 8, that more and more clusters have formed over the pores, providing further evidence for the assumption of gas transport and diffusion of species through the pores. In a more detailed analysis, a structure containing 24 at.% of bromine and no potassium was detected to penetrate the surface through a pore (Fig. 9). In addition to bromine, iron and chromium were also identified, giving a strong indication of metal bromide formation, either as iron bromide (FeBr_x) or as chromium bromide (CrBr_x). The standard enthalpies of formation for these



Fig. 6. An oxide cluster surrounded by pores at the surface of AISI 347 steel exposed to $[^{82}Br]KBr$ at 550 °C for 2 h.



Fig. 7. Pores piercing the surface oxide of AISI 347 steel exposed to $[\rm ^{82}Br]\rm KBr$ at 550 °C for 2 h.



Fig. 8. Iron oxide clusters (bright structures) and potassium chromate slates (darker structures) formed at the AISI 347 steel surface in an exposure with $[^{82}Br]KBr$ at 550 °C for 5 h.



Fig. 9. Metal bromide particle piercing the surface oxide of the AISI 347 steel in an exposure with $[^{82}Br]KBr$ at 550 °C for 5 h.

two bromides are very close to another [33], making it difficult to estimate, which bromides might have been formed. In an exposure to a gas containing bromine at a slightly higher temperature of 700 °C, FeBr₃ was reported to form first at the steel/oxide interface, followed by the formation of FeBr₂, CrBr₃, and NiBr₂ [34]. In the present study, although both chromium and iron were found in the clusters, the relative amount of chromium compared with iron was much higher than in the bulk material. CrBr₃ is stable also at 550 °C [35], so the high chromium concentration within the clusters could indicate the presence of CrBr₃ in larger quantities. The metal bromides form most likely beneath the surface at the steel/oxide interface, where the oxygen partial pressure is low. Then, the volatile bromides diffuse towards the steel surface, where they are oxidized, forming the cluster-like structures visible in Fig. 8.

After the eight-hour exposure, three distinct areas affected by KBr could be identified: heavily spalled area beneath the pellet; a K_2CrO_4 -rich region at the edge of the pellet, and the region further away from the pellet with less K_2CrO_4 particles (Fig. 10). The K_2CrO_4 particles formed furthest away were found more than three millimeters from the pellet edge. Since the exposure was carried out under flowing conditions and based on the constant distribution of the K_2CrO_4 particles at the steel surface, they have formed most likely through lateral diffusion of KBr rather than through gas-phase diffusion. The chromate formation is known to depend on the availability of oxygen from air, which together with the solid-solid contact at the pellet edge explains the vast number of formed K_2CrO_4 particles [36]. As mentioned before, the formation of metal bromides requires low oxygen pressures, which can be found underneath the KBr pellet. The spallation of the sample



Fig. 10. The AISI 347 steel surface after being exposed to $[^{82}\text{Br}]\text{KBr}$ at 550 $^\circ\text{C}$ for 8 h.

surface beneath the pellet originated most likely from the formation of metal bromides, which have oxidized rapidly while diffusing towards the steel surface, producing cracks in the original oxide and forming a new, yet porous oxide. Such an oxide possess very limited, if any, protective properties, which enables accelerated bromine transport to the steel/oxide interface as well as the increased interaction between potassium and the steel surface. It is worth mentioning, that the nickel content in the area exposed due to the spalling of the oxide was roughly 27 wt.%; three times the amount of nickel in the bulk steel. Very little bromine was detected in the same area, so although the formation of nickel bromide (NiBr₂) might occur [34], the increased nickel content resulted most likely from the selective bromination/oxidation of iron and chromium. A similar phenomenon has been observed with Fe-Cr-Ni alloys; the relative share of nickel just below the reacted zone increases as iron and chromium are selectively oxidized [37].

The initial step of the degradation process would be the chromate formation according to Eq. (1a). Whether molecular bromine or bromide anions form, is unclear. Nevertheless, the formed bromine species reacts further with iron and chromium found in the bulk material, forming metal bromides (Eq. 2). As these bromides oxidize, a porous and non-protective oxide forms (Eq. 3). Similarly, potassium chromate may react further to form non-protective chromium oxide. What happens to potassium and bromine after these reactions, needs to be studied in greater detail. Bromine could leave the reaction zone as molecular bromine, but the fate of potassium after the decomposition of K_2CrO_4 is still unclear.

 $Fe(s, in steel) + Br_2(g) \rightarrow FeBr_2(s)$ (2a)

 $2Cr(s, in steel) + 3Br_2(g) \rightarrow 2CrBr_3(s)$ (2b)

$$4FeBr_2(s) + 3O_2(g) \to 2Fe_2O_3(s) + 4Br_2(g)$$
(3a)

$$4CrBr_3(s) + 3O_2(g) \to 2Cr_2O_3(s) + 6Br_2(g)$$
(3b)

The whisker-like fine structures growing on the clusters were already observable after the two- and five-hour exposures (Figs. 6,8). The distinct morphology with pointy needle-like whiskers became more pronounced during the eight-hour exposure (Fig. 11). Based on the elemental analyses, the whiskers consisted of iron oxide. Similar structures, identified as hematite (Fe_2O_3) have been reported to form in the case of pure iron and iron-containing alloys [38–41]. Although the hematite whisker formation was then studied in the absence of KBr, the reaction between iron and oxygen is expected to occur in a similar manner in the present study, despite the presence of KBr.

The general features of the sample surface exposed to KBr for 12 h were similar to those detected after the eight-hour exposure and described above. Again, the formation of an iron-rich oxide and heavy



Fig. 11. Iron oxide formed onto the AISI 347 steel surface in an exposure with $[^{82}Br]KBr$ at 550 °C for 8 h.



Fig. 12. The porous AISI 347 steel surface (left) under a continuous K_2CrO_4 layer (right) after an exposure with $[^{82}Br]KBr$ at 550 °C for 12 h.

spallation was observed beneath the pellet, substantial K₂CrO₄ formation at the edge of the pellet, and minor K₂CrO₄ formation up to at least four millimeters away from the pellet. Instead of forming separate particles in the vicinity of the KBr pellet, K₂CrO₄ was found as continuous layers covering the steel surface (Fig. 12). The steel under the K₂CrO₄ layer was very porous and contained nickel up to 33 wt.%, almost four times the amount of nickel in the bulk material. It was this porous structure, where the high amount of ⁸²Br in Fig. 4d) was detected. The porosity and high nickel content of the steel beneath the reacted surface oxide provide further support for the idea of metal bromide formation and selective diffusion and oxidation of iron and chromium.

The presence of potassium chromate and metal bromides was verified also after the 24-hour exposure. This indicates that the KBr-induced high-temperature corrosion will proceed with both potassium and bromine having active roles in the reaction as long as KBr is available. The continuous K_2CrO_4 layer spread out for over 700 µm from the pellet edge (Fig. 13). During this longer exposure time, metal bromides are formed in the reaction between bromine and the steel, but whether K_2CrO_4 formed after 24 h originates from the reaction between potassium and the original surface oxide or between potassium and the formed porous chromium oxide, remained unclear.

4. Conclusions

The applicability of radioactive $[^{82}Br]KBr$ in high-temperature corrosion and diffusion studies was addressed in this work. An austenitic Nb-stabilized stainless steel was exposed to $[^{82}Br]KBr$ at 550 °C in



Fig. 13. The AISI 347 steel surface after being exposed to $[^{82}\text{Br}]\text{KBr}$ at 550 $^\circ\text{C}$ for 24 h.

flowing synthetic air for 2–24 hours. After the exposure, the radioactivity of the reacted steel surface was measured by a phosphor screen and the morphology and chemical composition of the reacted surface were analyzed by SEM. In addition, the possibility to produce [82 Br]KBr in a novel way by neutron activation at a cyclotron was studied.

Based on the results, the production of radioactive [⁸²Br]KBr by neutron activation is achievable. The radionuclidic purity of the produced [⁸²Br]KBr was very high and virtually no unwanted side reactions occurred during the process. The low activity and short half-life (35.3 h) of ⁸²Br make the produced [⁸²Br]KBr comparatively safe to use and suitable also for high-temperature studies.

The possibility to produce radioactive [⁸²Br]KBr by neutron bombardment will definitely decrease the manufacturing costs and through that, may open up new possibilities to use radioactive salts in research areas, which have not previously utilized such species. The sensitivity of the phosphorous film and its capability to clearly detect the remaining radioactivity even after a 24-hour exposure encourages further studies so that the method would one day be applicable for three-dimensional studies carried out by positron emission tomography (PET).

The KBr-induced high-temperature corrosion initiates through the simultaneous formation of solid potassium chromate (K_2CrO_4) and gaseous metal bromides. The chromate formation can be held responsible for depleting chromium from the surface oxide, thus converting it to an iron-rich, less protective oxide. Bromine diffuses towards the steel/oxide interface, where it forms gaseous metals bromides with iron and chromium at a low oxygen partial pressure. As these bromides diffuse towards higher oxygen partial pressures, they are rapidly oxidized, creating a porous non-protective oxide filled with pathways for accelerated gas transport and species diffusion. Local surface failure is supplemented by the oxidation of niobium, which breaks down the protective oxide. Niobium appears also to be involved in the pore formation, but its exact role remained unsolved.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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References

- L.L. Baxter, T.R. Miles, T.R. Miles Jr., B.R. Jenkins, T. Milne, D. Dayton, R.W. Bryers, L.L. Oden, The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences, Fuel Proc. Technol. 54 (1-3) (1998) 47–78.
- [2] L.A. Hansen, H.P. Nielsen, F.J. Frandsen, K. Dam-Johansen, S. Hørlyck, A. Karlsson, Influence of deposit formation on corrosion at a straw-fired boiler, Fuel Proc. Technol. 64 (1-3) (2000) 189–209.
- [3] B.-J. Skrifvars, R. Backman, M. Hupa, K. Salmenoja, E. Vakkilainen, Corrosion of super-heater steel materials under alkali salt deposits. Part 1: the effect of salt deposit composition and temperature, Corros. Sci. 50 (5) (2008) 1274–1282.
- [4] J. Krook, A. Mårtensson, M. Eklund, Metal contamination in recovered waste wood used as energy source in Sweden, Resour. Conserv. Recycl. 41 (1) (2004) 1–14.
- [5] K. Nakamura, S. Kinoshita, H. Takatsuki, The origin and behavior of lead, cadmium and antimony in MSW incinerator, Waste Manage. 16 (5-6) (1996) 509–517.
- [6] H. Belevi, H. Moench, Factors determining the element behavior in municipal solid waste incinerators. 1. Field studies, Environ. Sci. Technol. 34 (12) (2000) 2501–2506.
- [7] J. Vehlow, F.E. Mark, Influence of bromine on metal volatilization in waste combustion, J. Mater. Cycles Waste 2 (2) (2000) 89–99.
- [8] D. Bankiewicz, P. Vainikka, D. Lindberg, A. Frantsi, J. Silvennoinen, P. Yrjas, M. Hupa, High temperature corrosion of boiler waterwalls induced by chlorides and bromides – part 2: lab-scale corrosion tests and thermodynamic equilibrium modeling of ash and gaseous species, Fuel 90 (5) (2011) 2055–2063.
- [9] H. Wu, P. Yrjas, M. Hupa, Laboratory studies of potassium-halide-induced hightemperature corrosion of superheater steels. Part 1: exposures in dry air, Energy Fuel. 29 (2) (2015) 1186–1195.
- [10] H. Wu, D. Bankiewicz, P. Yrjas, M. Hupa, Laboratory studies of potassium-halideinduced high-temperature corrosion of superheater steels. Part 2: exposures in wet air, Energy Fuel. 29 (4) (2015) 2709–2718.
- [11] T.J. Ruth, The uses of radiotracers in the life sciences, Rep. Prog. Phys. 72 (1) (2008) 016701/1–016701/23.
- [12] R.B. Smith, L. Mcwhorter, J.W. Triplett, ⁸²Br-bromphenol blue: a potential hepatobiliary imaging agent. Organ distribution and biliary excretion in the rat, Int. J. Nucl. Med. Biol. 7 (1) (1980) 37–40.
- [13] S.P. Markey, R.W. Colburn, I.J. Kopin, Synthesis and purification of 2-bromo-αergocryptine-⁸²Br, J. Label. Compd. Rad. 12 (4) (1976) 627–630.
- [14] V.K. Sharma, H.J. Pant, S. Goswami, K.C. Jagadeesan, S. Anand, S. Chitra, Y.S. Rana, A. Sharma, T. Singh, H.G. Gujar, A. Dash, Production of gaseous radiotracers for industrial applications, Appl. Radiat. Isotopes 116 (2016) 110–119.
- [15] L. Vinnett, F. Contreras, A. Lazo, M. Morales, F. Diaz, K.E. Waters, The use of radioactive tracers to measure mixing regime in semi-autogenous grinding mills, Miner. Eng. 115 (2018) 41–43.
- [16] E. Plasari, E.J. Thereska, J.P. Leclerc, J. Villermaux, Tracer experiments and residence-time distributions in the analysis of industrial units: case studies, Nukleonika 44 (1) (1999) 39–58.
- [17] J.-H. Jung, S.-H. Jung, S.-H. Kim, S.-H. Choi, Synthesis and characterization of radioisotope nanospheres containing two gamma emitters, Appl. Radiat. Isotopes 70 (12) (2012) 2677–2681.
- [18] P. Fielitz, G. Borchardt, S. Ganschow, R. Bertram, A. Markwitz, ²⁶Al tracer diffusion in titanium doped single crystalline α-Al₂O3, Solid State Ionics 179 (11-12) (2008)

373-379.

- [19] St. Frank, U. Södervall, Ch. Herzig, Self-diffusion of Ni in single and polyctystals of Ni₃Al, Phys. Status Solidi B 191 (1) (1995) 45–55.
- [20] R.K. Collier, C.E. Backus, Direct measurement of cesium adsorption on high-temperature surfaces using radioactive tracers, Nucl. Technol. 31 (2) (1976) 279–281.
- [21] I. Villanueva, N. Heresi, P. Henriquez, P. Vega, Tracer techniques in the study of flow pattern in leaching tanks, Appl. Radiat. Isotopes 41 (10-11) (1990) 1159–1163.
- [22] W. Listwan, H. Dlugosz, J. Kras, L. Wallis, Radiotracer methods applied to diagnosis of technological installations, Nukleonika 33 (1-3) (1988) 3–22.
- [23] H. Siegel, A. Telfer, E.L. Bastin, Radioisotope tracing of oil refinery wastewater dilution, J. Water Pollut. Control Fed. 44 (8) (1972) 1637–1642.
- [24] B. Kharisov, O. Kharissova, U. Ortiz Mendez (Eds.), Radiation Synthesis of Materials and Compounds, CRC Press, Boca Raton, 2013.
- [25] S.-H. Jung, K.-I. Kim, J.-H. Ryu, S.-H. Choi, J.-B. Kim, J.-H. Moon, J.-H. Jin, Preparation of radioactive core-shell type ¹⁹⁸Au@SiO₂ nanoparticles as a radiotracer for industrial process applications, Appl. Radiat. Isotopes 68 (6) (2010) 1025–1029.
- [26] E.M. Dawed, K.K. Ben-Dalla, N.A. Salama, Production of ⁸²Br radioisotope, Al-Nawah 5 (5) (2004) 80–90.
- [27] V. Shivarudrappa, K.V. Vimalnath, High purity materials as targets for radioisotope production: needs and challenges, Bull. Mater. Sci. 28 (4) (2005) 325–330.
- [28] J. Lehmusto, D. Lindberg, P. Yrjas, L. Hupa, The effect of temperature on the formation of oxide scales regarding commercial superheater steels, Oxid. Met. 89 (1-2) (2018) 251–278.
- [29] J. Sui, J. Lehmusto, M. Bergelin, M. Hupa, The onset of potassium chloride induced high temperature corrosion: a novel experimental approach, Oxid. Met. 82 (5-6) (2014) 437–456.
- [30] M. Pons, M. Caillet, A. Galerie, High temperature oxidation of niobium superficially coated by laser treatment, Mater. Chem. Phys. 16 (5-6) (1987) 423–432.
- [31] E.N. Sheftel, O.A. Bannykh, Niobium-base alloys, Int. J. Refract. Met. H. 12 (5) (1993-1994) 303-314.
- [32] J. Lehmusto, B.-J. Skrifvars, P. Yrjas, M. Hupa, High temperature oxidation of metallic chromium exposed to eight different metal chlorides, Corros. Sci. 53 (10) (2011) 3315–3323.
- [33] M.W.M. Hisham, S.W. Benson, Thermochemistry of inorganic solids. 7. Empirical relations among enthalpies of formation of halides, J. Phys. Chem. 91 (13) (1987) 3631–3637.
- [34] S. Lee, S. Tsujikawa, Corrosion behavior of Fe-Cr and Fe-Ni-base commercial alloys in flowing Ar-42.6%O₂-14.7%Br₂ gas mixture at 700 °C, Mater. Corros. 48 (6) (1997) 364–371.
- [35] R.J. Sime, N.W. Gregory, Vaporization of chromium(III) bromide. Evidence for chromium(IV) bromide, J. Am. Chem. Soc. 82 (1) (1960) 93–96.
- [36] J. Lehmusto, M. Bergelin, J. Sui, J. Juhanoja, B.-J. Skrifvars, P. Yrjas, Applicability of ToF-SIMS and stable oxygen isotopes in KCl-induced corrosion studies at high temperatures, Corros. Sci. 125 (2017) 1–11.
- [37] J. Lehmusto, P. Yrjas, B.-J. Skrifvars, M. Hupa, High temperature corrosion of superheater steels by KCl and K₂CO₃ under dry and wet conditions, Fuel Proc. Technol. 104 (2012) 253–263.
- [38] I. Svedung, B. Hammar, N.-G. Vannerberg, The effect of recrystallization on the oxide scale composition and growth of whiskers during the oxidation of pure iron, Oxid. Met. 6 (1) (1973) 21–44.
- [39] M. Shao, M. Kwauk, Oxidation of TiAl, Ni and Fe in a dynamic environmental SEM, China Part. 2 (1) (2004) 31–36.
- [40] N. Bertrand, C. Desgranges, D. Poquillon, M.C. Lafont, D. Monceau, Iron oxidation at low temperature (260–500 °C) in air and the effect of water vapor, Oxid. Met. 73 (1-2) (2010) 139–162.
- [41] N.F. Garza-Montes-de-Oca, J.H. Ramírez-Ramírez, I. Alvarez-Elcoro, W.M. Rainforth, R. Colás, Oxide structures formed during the high temperature oxidation of hot mill work rolls, Oxid. Met. 80 (1-2) (2013) 191–203.