Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Nuclear Materials 329–333 (2004) 1353–1356
journal of nuclear materials
www.elsevier.com/locate/jnucmat

# Methods for the mitigation of the chemical reactivity of beryllium in steam

F. Druyts [a,*], E.C. Alves [b], C.H. Wu [c]

[a] SCK • CEN, The Belgian Nuclear Research Centre, Boeretang 200, B-2400 Mol, Belgium
[b] Instituto Tecnológico e Nuclear, Departamento de Física, Estrada Nacional 10, P-2686-953 Sacavém, Portugal
[c] European Fusion Development Agreement, Max-Planck-Institut für Plasmaphysik, Boltzmanstrasse 2,
D-85748 Garching bei München, Germany

---

## Abstract

In the safety assessment of future fusion reactors, the reaction of beryllium with steam remains one of the main concerns. In case of a loss of coolant accident (LOCA), the use of beryllium in combination with pressurised water as coolant can lead to excessive hydrogen production due to the reaction $Be + H_2O = BeO + H_2 + heat$. Therefore, we started an R&D programme aimed at investigating mitigation methods for the beryllium/steam reaction. Beryllium samples were implanted with either calcium or aluminium ions in a 210 kV ion implanter at ITN Lisbon. The chemical reactivity of these samples in steam was measured at SCK • CEN in a dedicated experimental facility providing coupled thermogravimetry/mass spectrometry. In comparison to reference undoped material, the reactivity of doped beryllium after 30 min of exposure decreased with a factor 2 to 4. The mitigating effect was higher for calcium-doped than for aluminium-doped samples.

---

## 1. Introduction

The use of beryllium as a plasma-facing component or neutron multiplier in fusion reactors in combination with pressurised water as coolant, may, in case of a loss of coolant accident (LOCA), lead to the highly exothermal reaction between hot beryllium and steam, producing hydrogen gas ($Be + H_2O = BeO + H_2 + heat$). Therefore, in view of the intrinsic safety of ITER for example, it is desirable to restrict the reaction between beryllium and steam. Therefore, in the framework of the European Fusion Development Agreement (EFDA), we initiated a research programme aimed at identifying and testing mitigation methods for the beryllium/steam reaction.

The oxidation mechanism of beryllium in steam depends strongly on temperature [1–3]. In the temperature range applicable to fusion reactor applications (up to 600 °C) the rate-determining step in the oxidation of beryllium in steam is the diffusion of $Be^{++}$ through the oxide layer. In this case, classical diffusion theory predicts a parabolic kinetics. This has been confirmed experimentally by diverse research groups in the framework of fusion reactor materials research (see for example [4,5]). Mitigation strategies should therefore be aimed at hampering the effective diffusion of $Be^{++}$. There are experimental indications that the alloying of beryllium is the most promising method to reduce the reaction kinetics of beryllium in steam. In this study, we investigated the influence of calcium and aluminium on the oxidation kinetics [6].

## 2. Experimental details

### 2.1. Investigated material

At the Instituto Tecnológico e Nuclear in Lisbon, Portugal, beryllium samples were implanted with either

---

[*] Corresponding author. Tel.: +32-14 33 3238; fax: +32-14 32 3553.
*E-mail address:* fdruyts@sckcen.be (F. Druyts).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.04.204

aluminium or calcium ions. For this purpose, we used half tensile specimens fabricated from grade S-65C beryllium. Table 1 summarises the main impurities in this material. The equipment consisted of a 2.5 MeV van de Graaff accelerator and a 210 kV high fluence ion implanter. Beryllium samples were implanted with either Al or Ca with different energies and fluences to achieve a broad depth spectrum. Al ions were implanted with 70, 50, and 25 keV, with nominal fluences of $1\times10^{17}$, $5\times10^{16}$ and $1\times10^{16}/\text{cm}^2$, respectively. The maximum of the implanted profile was centred at 125 nm. Ca ions were implanted with 80 and 40 keV with fluences of $2\times10^{17}$ and $5\times10^{16}/\text{cm}^2$, respectively. The maximum of the implanted profile was centred at 90 nm. In both cases the measured amount of Al and Ca in the samples agrees with the nominal value. All the implantations were done at room temperature and the current density was kept below 0.5 $\mu\text{A/cm}^2$ in order to avoid beam heating. The RBS spectra of the implanted samples, obtained with a 2.0 MeV $\text{He}^+$ beam and a solid state detector placed at 140° with respect to the incident beam, are displayed in Fig. 1 together with a not implanted sample. Notice that the height of the peaks in the figure must be normalized to the Rutherford cross sections in order to be comparable. According to the experimental data we calculated a maximum concentration of 15 at.% for Ca and 8 at.% for Al in the implanted region. A relevant feature of the results is the higher oxygen content in the Ca implanted samples compared to the Al and not implanted sample. Although in residual concentrations we must refer to the presence of several impurities, besides C and O, being the more important P and Ni.

Table 1
Main impurities in the investigated beryllium (wt%)

| | |
|---|---|
| BeO | 0.6 |
| Fe | 0.06 |
| Al | 0.02 |
| Si | 0.03 |
| Mg | <0.01 |
| C | 0.03 |

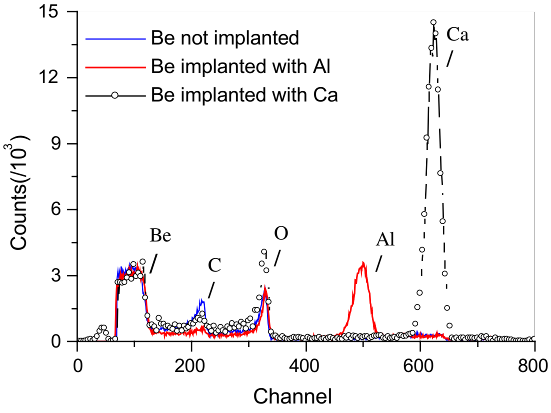

Fig. 1. RBS spectra of the implanted samples and a reference RBS spectrum of a non-implanted beryllium sample.

### 2.2. Chemical reactivity measurements

The chemical reactivity of doped and reference non-doped beryllium specimens was determined at SCK • CEN, Mol, Belgium, in a dedicated experimental facility consisting of steam-generating equipment, a system for combined thermogravimetry/differential thermal analysis (TG/DTA), and a quadrupole mass spectrometer.

Fig. 2 shows a schematic representation of the experimental setup. The steam generator system is set to deliver a flow of 0.075 ml/min of $H_2O$ to the evaporator oven, where steam is produced and subsequently carried to the TG/DTA furnace by a 50 ml/min argon flow. The beryllium sample is placed in a cylindrical alumina crucible inside the TG/DTA furnace. The gas mixture leaving the TG/DTA furnace after reaction with the beryllium sample (consisting of hydrogen, argon, and excess steam) is led through two condensers operating at 5 and −5 °C respectively to remove excess steam. The dry gas mixture then enters the ionisation chamber and the quadrupole mass spectrometer, where the heights of the mass 2 (hydrogen) and mass 40 (argon) peaks are measured. The quadrupole mass spectrometer is calibrated with reference mixtures of between 100 and 30 000 ppm $H_2$ in argon. Using the thus established calibration line, we relate the mass 2/mass 40 peak height ratio to the hydrogen concentration in the argon flow reaching the mass spectrometer. Knowing the argon mass flow, we can then calculate the hydrogen generation rate.

## 3. Experimental results and discussion

To investigate the influence of ion-implantation on the oxidation kinetics of beryllium in steam, we investigated a non-implanted reference sample, a calcium-implanted sample, and an aluminium-implanted sample. The limited number of test specimens was due to the high cost of ion implantation. As the test temperature we chose 650 °C, which is still within the region of parabolic kinetics, and offers the advantage of a relatively fast kinetics as opposed to lower temperature points. Fig. 3 shows the mass spectrometry results for the aluminium-doped specimen. The upper graph presents the instantaneous hydrogen production as measured by the mass spectrometer, either in terms of the mass 2/mass 40 ratio (left axis) or, after application of the calibration line, in terms of the $H_2$ concentration in

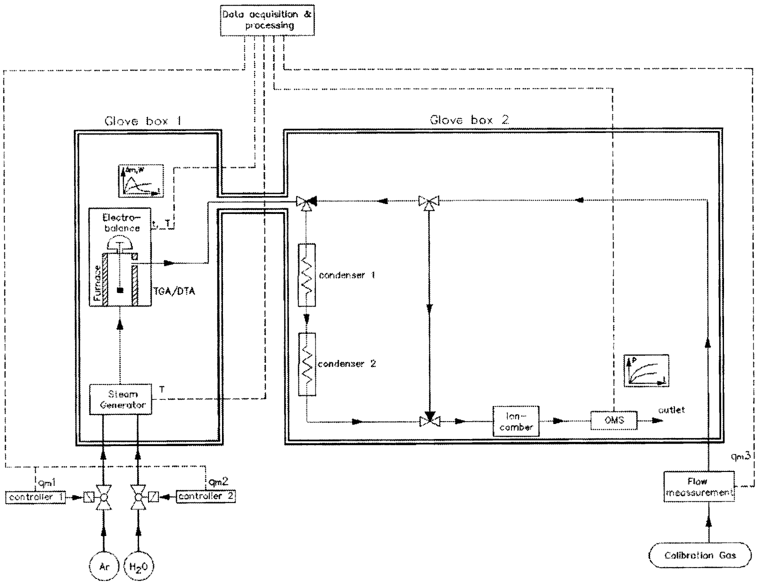

Fig. 2. Schematic representation of the experimental setup.

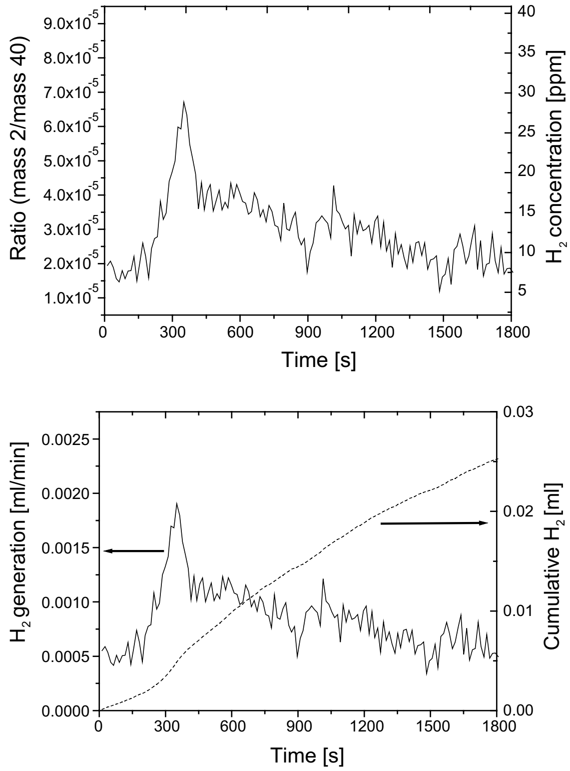

Fig. 3. Mass spectrometry results for an aluminium-doped beryllium half tensile specimen exposed to steam at 650 °C. The upper graph shows the instantaneous hydrogen production as a function of time. The lower graph shows the hydrogen generation rate (solid line) and the accumulated hydrogen production (dashed line).

argon. The lower graph presents the hydrogen generation rate in ml/min. Integration yields the accumulated hydrogen production in milliliters.

Fig. 4 compares the chemical reactivity of doped material with reference undoped beryllium. After 30 min of exposure we see a reduction of chemical reactivity by a factor 2 through Al-doping and through a factor 4 for Ca-doping. This seems to indicate an effect of ion implantation on the oxidation kinetics. However, additional experiments would be needed to validate the mitigating trend at longer exposure times. If this effect is confirmed, then methods for metallurgical doping need

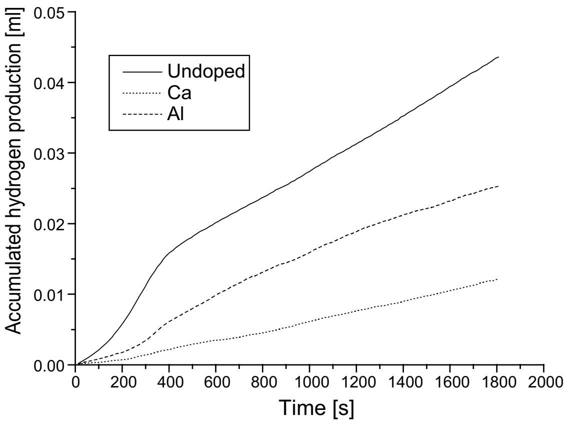

Fig. 4. Influence of calcium and aluminium doping on the chemical reactivity of beryllium during the first 30 min of exposure to steam at 650 °C.

to be pursued, as direct oxide doping by ion-implantation is too expensive to produce large volumes of beryllium.

## 4. Conclusions

We investigated the influence of doping on the chemical reactivity of beryllium in steam. For this purpose, we ion-implanted beryllium samples with aluminium and calcium ions respectively and exposed the samples to steam at 650 °C in an experimental facility containing TG and mass spectrometry equipment. The ion-implantation resulted in a reduction of the chemical reactivity by a factor 2 for aluminium-doped material and by a factor 4 for calcium-doped material.

## Acknowledgements

The authors wish to thank Ing. Steven Smets and Mr Kris Penasse for their technical assistance. This work has been partly financed by the European Commission in the framework of the European Fusion Development Agreement. However, the content of the publication is the sole responsibility of its publishers and it does not necessarily represent the views of the Commission or its services.

## References

[1] O. Kubaschewski, B.E. Hopkins, Oxidation of Metals and Alloys, Butterworth, London, UK, 1962.
[2] I.I. Papirov, Oxidation and Protection of Beryllium, Edited Translation, FTD Wright-Patterson, FTD-HT-23-110-69, Ohio, USA, 1969.
[3] D.A. Petti, G.R. Smolik, R.A. Anderl, J. Nucl. Mater. 283–287 (2000) 1390.
[4] F. Druyts, J. Fays, C.H. Wu, Fusion Eng. Des. 63&64 (2002) 319.
[5] R.A. Anderl, F. Scaffidi-Argentina, D. Davydov, R.J. Pawelko, G.R. Smolik, Proceedings of the 4th IEA International Workshop on Beryllium for Fusion Technology, p. 62.
[6] F. Druyts, Proceedings of the 4th IEA International Workshop on Beryllium for Fusion Technology, p. 70.