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Original Article

High-temperature interaction of oxygen-preloaded Zr1Nb alloy with nitrogen

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ABSTRACT

Potential air ingress scenarios during accidents in nuclear reactors or spent fuel pools have raised the question of the influence of air, especially of nitrogen, on the oxidation of zirconium alloys, which are used as fuel cladding tubes and other structure materials. In this context, the reaction of zirconium with nitrogen-containing atmospheres and the formation of zirconium nitride play an important role in understanding the oxidation mechanism. This article presents the results of analysis of the interaction of the oxygen-preloaded niobium-bearing alloy M5[®] with nitrogen over a wide range of temperatures (800–1400°C) and oxygen contents in the metal alloy (1–7 wt.%). A strongly increasing nitriding rate with rising oxygen content in the metal was found. The highest reaction rates were measured for the saturated α -Zr(O), as it exists at the metal–oxide interface, at 1300°C. The temperature maximum of the reaction rate was approximately 100 K higher than for Zircaloy-4, already investigated in a previous study [1]. The article presents results of thermogravimetric experiments as well as posttest examinations by optical microscopy, scanning electron microscopy (SEM), and microprobe elemental analyses. Furthermore, a comparison with results obtained with Zircaloy-4 will be made.

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1. Introduction

Zirconium alloys are used worldwide in the nuclear industry for fuel claddings and other structural materials because of their good mechanical properties and corrosion resistance at operational conditions as well as because of their low cross section for thermal neutrons. However, during loss-of-coolant accidents as well as severe nuclear accidents, the high-temperature oxidation of zirconium by water steam causes serious degradation of the mechanical properties of cladding tubes, resulting in the loss of barrier effect against the release of fission products, as well as in the production of hydrogen and chemical heat. The hydrogen source term due to the zirconium-steam reaction carries the risk of hydrogen detonation, as was seen during the Fukushima Daiichi accidents. The chemical heat produced by the oxidation reaction may exceed the nuclear decay heat at high temperatures, thus becoming a driving force for thermal excursions of the reactor core [2].

Numerous studies on the oxidation of zirconium alloys in water steam have been conducted over a wide range of temperatures and conditions during the last decades, mainly triggered by the TMI-2

accident 1979 in the United States [3,4]. Air ingress scenarios in reactors have also been discussed for a long time; see for example the study by Powers et al. [5]. After the Fukushima accidents, air ingress accident scenarios for spent fuel pools came into focus for international research [6].

It is known from many experimental studies that the oxidation of zirconium alloys by steam or oxygen is strongly affected by the presence of nitrogen [7] [8–12]. Especially in the temperature range between 800°C and 1200°C, the reaction kinetics are strongly increased by nitrogen, resulting in more severe degradation of the cladding and higher hydrogen source terms (if steam is available) compared to oxidation in pure steam and oxygen atmosphere. The understanding of the mechanism of nitrogen attack is that zirconium nitride, ZrN, is temporarily formed and subsequently reoxidized; this is connected with serious volume mismatches because of the different densities of the involved phases, and with this the formation of non-protective oxide scales. Furthermore, it is known that, on the one hand, the reaction of zirconium with nitrogen is very slow due to the formation of a thin protective nitride scale and low diffusion coefficients of nitrogen in Zr [13], but, on the other hand, much ZrN is formed during the reaction of oxygen-stabilized zirconium with nitrogen [9]. Conditions favorable for the formation of ZrN are present locally at the metal–oxide interface after consumption of oxygen when nitrogen is in contact with the oxygen-

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stabilized α -Zr(O) phase. The results of a systematic study of the interaction between oxygen-stabilized α -Zr(O) prepared from the tin-bearing alloy Zircaloy-4 with nitrogen has been published recently; this study showed a strong influence of the oxygen content in the metal, and of the temperature, on the reaction kinetics with nitrogen [1]. This article presents results of complementary experiments with the niobium-bearing alloy M5[®], produced by AREVA (France).

2. Experimental details

2.1. Test setup

All experiments presented in this article were conducted in a commercial thermal balance (NETZSCH STA-409) with a vertical tube furnace and balance below the furnace, coupled via a capillary with a quadrupole mass spectrometer (NETZSCH Aeolos); details are described in the study by Steinbrück et al. [14]. The gases (Ar, O₂, N₂) were supplied via Bronkhorst[®] flow controllers at the lower part of the vertical tube furnace. Argon flowed through the balance containment into the furnace; the reaction gases were directly injected into the reaction tube to prevent contamination of the balance and to ensure a well-defined gas mixture in the furnace. All gases used were highly pure, with less than one and 10 ppm impurities, respectively.

2.2. Specimens

M5[®] is an advanced cladding alloy produced by AREVA for pressurized water reactors; it has approximately 1 wt.% niobium and 0.13 wt.% oxygen as main alloying components. Tube segments 2 cm long (10.75 mm outer diameter and 0.725 mm wall thickness) were cut from longer tubes, deburred and ground at both ends, and cleaned in an ultrasonic bath of acetone. The samples were positioned vertically on an yttrium oxide plate in the furnace of the thermal balance. Tubes were open at the ends; consequently, reactions of the gases with the inner and outer surface of the tube segments were possible, but with different thermohydraulic boundary conditions due to the bottom-up gas flow.

2.3. Test procedure

The objective of this study was the investigation of the α -Zr(O) reaction with nitrogen as a function of temperature and oxygen content of the metal in the whole phase region of α -Zr(O). Reasonable reaction rates were achieved at temperatures from 800°C; the upper temperature limit was 1400°C. The test matrix is shown by red dots in the Zr-O phase diagram [15] in Fig. 1.

Argon was used as carrier gas and reference gas for mass spectroscopy in all tests. This will be not explicitly mentioned in the rest of the article. The use of argon may have some influence on gas diffusion, especially in pores and cracks. Investigation of such an effect was not within the scope of the report. The argon flow rate during all tests was 3 l/h. The flow rate of oxygen during preoxidation (PO) was 1–3 l/h; that for nitrogen during the nitriding phase was 10 l/h.

As shown in Fig. 2, the specimens were subjected to (1) slow and manually controlled PO in oxygen at 1200°C until the desired mass gain was obtained, leading to a circumferentially and axially homogeneous oxygen uptake, (2) 3 hour of homogenization in argon at 1400°C, and (3) 1 hour of reaction at the predefined temperature (800–1400°C) in nitrogen. The use of oxygen (instead of water steam, which for nuclear accidents would be more prototypical) allowed in-situ preparation and investigation within one thermogravimetric (TG) experiment. In any case, hydrogen, possibly taken up during PO in steam, would have been completely released during the homogenization phase according to Sieverts' law [16]. Fig. 3 shows two micrographs with through-wall cross section taken after the preoxidation and after the homogenization phase, proving the dissolution of the oxide scale during 3 hour at 1400°C in inert atmosphere. Owing to the short duration of the oxidation phase and the low oxygen mass flow rate, the tube segment was only oxidized externally at the points to which oxygen had direct access.

2.4. Posttest examinations

Macro photos were taken of all specimens after the tests. Then, the specimens were embedded in epoxy resin, cut, ground, and polished for metallographic examination by optical microscopy. The local composition of selected samples, especially with regard to

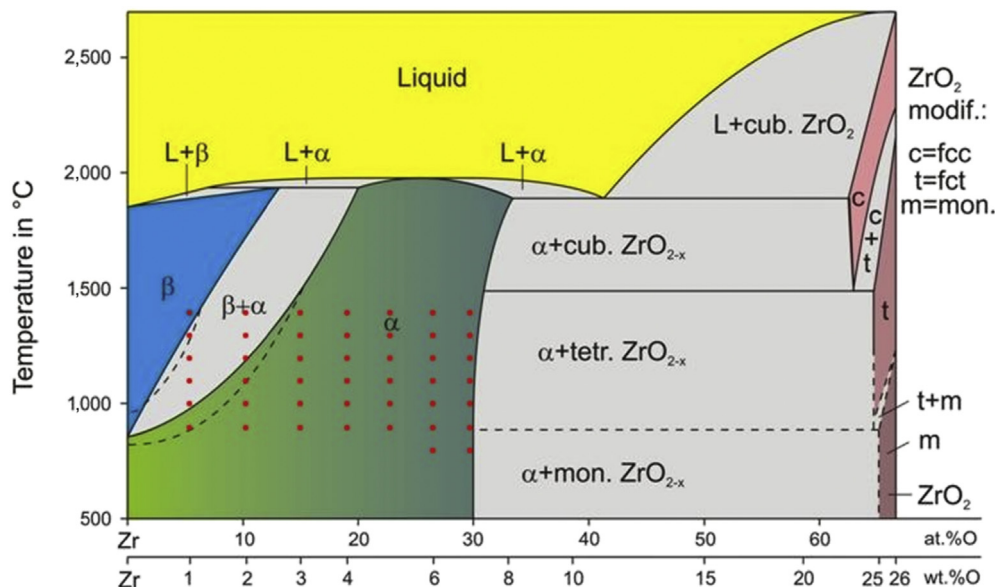


Fig. 1. Phase diagram Zr-O [15] with test matrix shown by red dots.

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