Scripta Materialia 117 (2016) 20–23

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Creep flow and fracture behavior of the oxygen-enriched alpha phase in zirconium alloys

R. Chosson [a,b,*], A.F. Gourgues-Lorenzon [a], V. Vandenberghe [c], J.C. Brachet [b], J. Crépin [a]

[a] MINES ParisTech, PSL Research University, Centre des Matériaux, UMR CNRS 7633, BP 87, 91003 Evry Cedex, France
[b] CEA Saclay, DEN/DMN/SRMA, 91191 Gif-sur-Yvette Cedex, France
[c] CEA Saclay, DEN/DMN/SEMI, 91191 Gif-sur-Yvette Cedex, France

ARTICLE INFO

Article history:
Received 20 January 2016
Received in revised form 15 February 2016
Accepted 16 February 2016
Available online 27 February 2016

Keywords:
Zirconium alloys
Creep
High temperature deformation
Oxidation
Embrittlement

ABSTRACT

During hypothetical Loss-Of-Coolant-Accident (LOCA) scenario, zirconium alloy fuel cladding tubes are exposed to internal pressure and high temperature oxidation, so that an oxygen-stabilized α(O) phase, forms from the outer surface of the cladding, under the zirconia oxide layer. The high-temperature viscoplastic flow and fracture behavior of the α(O) phase were characterized through axial creep tests performed under vacuum, on representative model materials containing 10–30 at.% of oxygen. Creep strengthening and ductile-to-brittle transition were quantified as a function of oxygen content and test temperature, and modeled into viscoplastic flow constitutive equations and an empirical fracture criterion.

1. Introduction

The hexagonal close-packed alpha (α) phase of Group 4 elements — titanium, zirconium and hafnium — can dissolve up to 30 at.% interstitial oxygen [1–3]. It exhibits a high chemical affinity for oxygen and in oxidizing environments, an oxygen-stabilized α phase easily forms at high temperature from the body centered cubic β phase [4], leading to e.g. the so-called "alpha-case" in Ti alloys. Such high amounts of oxygen deeply alter the mechanical behavior of the α phase and lead to a progressive transition of its mechanical behavior from that of a metal to that of an oxide. In Ti alloys, this phase is very detrimental to ductility, fatigue and creep lifetime up to 600 °C [5]. The oxygen-enriched α phase of Zr alloys, called α(O), is also brittle at room temperature from 0.5 wt.% oxygen [6]. The high-temperature mechanical behavior of oxygen-enriched Zr alloys has been reported from compression tests and tensile creep tests [7–9]. A significant increase in the compressive steady-state flow stress with increasing oxygen content has been reported, in a linear [7] or an exponential manner [9], for test temperatures between 750 °C and 1200 °C and for amounts of oxygen up to 2 wt.%. From tensile creep tests on Zircaloy-2 and Zircaloy-4 enriched in oxygen, similar oxygen-induced exponential strengthening of the α phase was reported between 700 and 1400 °C for contents up to 1.5 wt.% [10,11]. The following empirical relationship has been proposed to describe such effect:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp(-Bc) \quad (1)$$

In Eq. (1), $\dot{\varepsilon}_0$ and $\dot{\varepsilon}$ are the steady-state viscoplastic strain rates (s^{-1}) of an oxygen-free and of an oxygen-enriched material, respectively, for the same values of applied stress and temperature; c is the oxygen concentration (wt.%) and B is an adjustable material parameter. The value of B was set to 3.2 in enriched Zircaloy-4 [10] and to 2.8 in enriched Zircaloy-2 [11]. To the authors' knowledge, the viscoplastic flow behavior for oxygen contents beyond 2 wt.% is still unknown while the solubility of oxygen in α phase can reach 7 wt.%. In addition, the ductility of α(O) containing up to 1.5 wt.% O has never been reported above 750 °C.

The present study focuses on the viscoplastic flow and fracture behavior of the α(O) phase in a Zr alloy, to identify viscoplastic flow regimes and, if any, creep ductility temperature and composition ranges between 2 and 5.8 wt.% O and between 800 and 1100 °C.

2. Experimental details

Model oxygen-enriched specimens were produced from as-received M5® (Zr-1%Nb-0.14%O) alloy thanks to a two-step procedure. The specimens were 265-mm-long tubes with 9.5 mm in outer diameter and 0.57 mm in thickness. They were first oxidized in steam in the EDGAR facility [12] in order to add the required 2 (10), 3.2 (16), 4.3 (20) and

* Corresponding author at: Areva NP, E&P Division, 10 rue Juliette Récamier, 69006 Lyon, France.
E-mail address: raphael.chosson@areva.com (R. Chosson).

http://dx.doi.org/10.1016/j.scriptamat.2016.02.021
1359-6462/

5.8 (26) wt.% (at.%) oxygen content to the material, mainly as zirconia and α(O) phase outer layers of a few tens of μm in thickness. Oxidized specimens were then fitted to an electro-mechanical tensile machine operated under secondary vacuum and as described by Kaddour et al. [13]. The load was applied along the tube axis. The procedures used for temperature monitoring with spot-welded thermocouples and axial elongation measurement by laser extensometry were the same as in [13].

Annealing the specimens at 1200 °C under secondary vacuum allowed dissolution of zirconia and diffusion of oxygen across the wall [6], leading to a bulk α(O) microstructure by transformation from the β phase. Due to the high temperature oxidation/annealing heat-treatment, the produced model materials strongly differ from the original M5® alloy and consequently will be called Zr-1%Nb-*c*%O hereafter, where *c* is the oxygen concentration in wt.%.

Right after the annealing stage, the temperature was decreased down to the value selected for the creep test (Fig. 1a), thus avoiding going down to room temperature, at which the α(O) phase is brittle. Several constant load levels were successively applied to a given specimen as in [13]. For each load level, the steady-state true strain rate was measured. None or very limited primary creep was observed. Tests were performed between 800 and 1000 °C for true axial stresses between 2 and 31 MPa. The influence of the loading history was checked to be negligible (within the experimental uncertainties) by increasing, then decreasing load levels on one specimen.

From tested specimens, samples were extracted, polished and etched using in-house preparation procedures [14] and observed by optical and scanning electron microscopy (SEM). Oxygen quantification was systematically done on each tested specimen, using electron probe microanalysis (EPMA), with a ± 0.1 wt.% accuracy thanks to an in-house procedure for correction of oxygen contamination artifacts [14]. The average texture was determined by neutron diffraction on 10-mm-long samples containing about 10^6 grains.

3. Experimental results and discussion

3.1. Microstructure of the model materials

As illustrated in Fig. 1b, the microstructure of the oxygen-enriched specimens is mainly composed of coarse α(O) grains. Their size (30 to 300 μm) is much larger than that of the starting material (6 μm). The amount of untransformed β phase during the creep test depends on the test temperature and oxygen content. It reaches 15 ± 5% at 1100 °C in Zr-1%Nb-2%O and is lower than 10% for lower test temperatures or higher oxygen contents, in agreement with literature, as detailed in [15]. Uniform distribution of oxygen across the wall was confirmed by EPMA, with a variation by less than 15%. The residual regions transformed from β phase after final cooling were strongly enriched in Nb and Fe but only contained 0.5 ± 0.2 wt.% of oxygen. Oxygen-enriched specimens exhibited a strong average texture, different from the one of the as-received alloy. The Kearns parameter along the axial and tangential directions were 0.41 and 0.44 ± 0.05 respectively, compared to 0.66 and 0.23 ± 0.05 for the as-received alloy.

3.2. Viscoplastic flow behavior

Fig. 2 summarizes the viscoplastic flow behavior for 2 and 3.2 wt.% enriched specimens. A brittle behavior was observed for oxygen content higher than 4 wt.%, without significant strain. Experimental scattering in strain rates was less than a factor 2 at high stresses and less than 50% at low stresses.

For the first time, two viscoplastic flow regimes have been evidenced in an oxygen-enriched zirconium alloy. For all temperatures and at higher stresses (>15 MPa), a typical power-law regime is observed, with a stress power-law exponent, *n*, close to 5. At 1000 and 1100 °C, data at lower stresses (<10 MPa) are consistent with a near-linear flow regime. At 900 °C, data show a transition in the *n* exponent at lower stresses, possibly to a near-linear regime.

The power-law regime at higher stresses is consistent with viscoplastic strain regimes controlled by glide and climb of dislocations already reported in pure zirconium and its alloys (*n* ranging from 4 to 7 [13,16,17]) and in oxygen-enriched zirconium alloys ($n \approx 5.4$ [10,11]). The near-linear regime is consistent with diffusional flow regimes, already observed in un-enriched α phase at lower temperature [13,17,18]. However the average grain size in Zr-1%Nb-2/3.2%O is large (100 μm) and therefore the near-linear viscoplastic regime could possibly be controlled by a Harper–Dorn mechanism [19]. Materials with various grain sizes should allow ascertaining the actual physical viscoplastic deformation mechanism in these conditions.

Using the creep-rate equations established for un-enriched single phases of two zirconium alloys [13] enables us to point out the strengthening effect of oxygen. This comparison was made despite the difference in texture of both kinds of materials, as the strain anisotropy of the α phase might be low at such high temperatures [20]. As this phase is not stable at high temperature without oxygen addition, its mechanical behavior has to be extrapolated up to 1000 °C for comparison with the present results. Zr-1%Nb-2/3.2% alloys exhibit a much higher resistance to viscoplastic strain (×100 to ×1000) than that predicted for the α phase of un-enriched alloys.

For comparison purposes the creep-rate equations established between 800 and 1000 °C by Chow et al. [11] on up to 1.5 wt.% oxygen-enriched Zircaloy-4 were extrapolated to higher oxygen contents. In the higher stress domain, strain rate predictions obtained in this way are five times higher than those measured for Zr-1%Nb-2%O but are close to the ones obtained for Zr-1%Nb-3.2%O. Because of the transition to a near-linear viscoplastic regime, strain rate predictions based on the results of Chow et al. are not relevant in the lower stress regime.

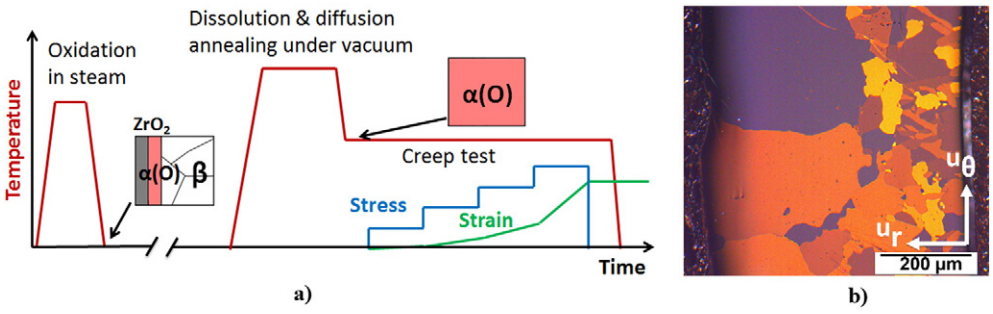

Fig. 1. a) Principle of fabrication and thermal-mechanical testing of the Zr-1%Nb-c%O specimens, with schematic structures of the wall-thickness of the cladding (outer surface on the left), b) Optical micrograph of a Zr-1%Nb-3.2%O cladding specimen tested at 1000 °C.