Journal of Nuclear Materials 511 (2018) 18–29

Contents lists available at ScienceDirect

Journal of Nuclear Materials

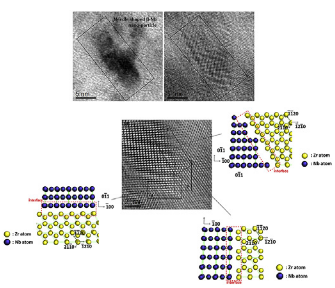
journal homepage: www.elsevier.com/locate/jnucmat

Shape, orientation relationships and interface structure of beta-Nb nano-particles in neutron irradiated zirconium alloy

J. Ribis*, S. Doriot, F. Onimus

DEN-Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 April 2018
Received in revised form
20 July 2018
Accepted 21 August 2018
Available online 24 August 2018

Keywords:
Zirconium alloys
Nanoparticles
Interface structure
High-resolution electron microscopy
Irradiation effect

ABSTRACT

Under neutron irradiation, radiation enhanced beta-Nb nano-precipitates develop within the α-grains of the Zr-Nb alloys. This radiation enhanced precipitation is of great interest since it may have some influence on the post-irradiation mechanical behavior of the material. In this paper the shape, the orientation relationship and the interface structure of such nano-particles are studied by means of both conventional and high-resolution transmission electron microscopy. The radiation damage was annealed out, thanks to a prior heat treatment and a creep test, in order to easily observe the beta-Nb nano-particles. The nano-particles exhibit a needle-like shape with a short thickness along the c-direction of 1.5 nm on average, a length and a width respectively of 6 nm and 3 nm, on average, in the basal plane. Using high-resolution TEM, a near Pitsch-Schrader orientation relationship is identified for a nano-particle. The interface atomic structure at various locations around the nano-particle has been accurately determined and an atomic model of the interface structure has been proposed.

1. Introduction

Zirconium alloys are commonly used in Pressurized Water Reactors, as cladding tubes of the nuclear fuel owing to their excellent properties for nuclear applications. In-reactor, the components made of zirconium alloys are subjected to high irradiation doses. Hence, the understanding of neutron irradiation effects on zirconium alloys is an important step toward the prediction of the integrity of these components. Among the wide variety of zirconium alloys, the Zr-Nb alloys are extensively used for their good corrosion resistance [1–3].

In the M5™ alloy, which contains 1%wt of Nb, part of the Nb atoms are in substitutional solid solution. Because the solubility limit of Nb in alpha-Zr is always lower than 1%wt [2,4] the remaining Nb atoms form a homogeneously refined dispersion of beta-Nb precipitates [5]. These native beta-Nb precipitates have the

* Corresponding author.
E-mail address: joel.ribis@cea.fr (J. Ribis).

https://doi.org/10.1016/j.jnucmat.2018.08.042
0022-3115/

size of 50 nm and a b.c.c. lattice with the parameter a = 0.328 nm [6].

In fact, after processing, the concentration of Nb in solid solution in the Zr matrix corresponds to the maximum solubility near the monotectoid temperature, which is higher than the solubility at the service temperature (623 K). Owing to the slow diffusion of Nb, the equilibrium microstructure cannot be reached thermally during the cooling down after the heat treatment. The alpha-Zr matrix therefore exhibits a slight super-saturation of Nb atoms. As pointed out in Ref. [7], only very long term annealing treatments (up to 20000 h) allow reaching the thermodynamics equilibrium at temperatures below 853 K.

Interestingly, after a few years in reactor, a high density of nano-precipitates is observed [5,6,8–10] that are suspected to influence the corrosion [10] or the growth behavior [5] of the material under irradiation. These nano-precipitates are usually imaged using the g = 0002 diffraction vector. In this condition, the numerous and small <a>-loops disappear, allowing an easy observation of other microstructural features such as the nano-precipitates. According to Doriot et al. [5], the nano-particles look circular, with diameter close to 3 nm for fluences lower than 3×10^{25} n/m^2, and are randomly dispersed. For further irradiation dose, they gradually tend to concentrate within 50 nm spaced layers parallel to the basal plane, and some of them become elongated in the direction close to the basal plane trace. The average width of these needle shaped precipitates is between 1 and 3 nm and the length increases up to 12 nm (6 nm long on average) [11–13]. This very peculiar shape has to be attributed to the effect of irradiation since, after thermal annealing only, for 1500 h at temperature up to 770 K, this shape and size of beta-Nb precipitate is never observed [14]. It is also shown that these nano-precipitates are thermodynamically stable since they do not disappear after annealing, at least after heat treatments up to 770 K [11]. This suggests that they result from the radiation-enhanced diffusion of Nb due to the high concentration of vacancies under irradiation [8]. Indeed, since the as-received Zr-1% Nb alloy consists in a α-phase matrix supersaturated in Nb atoms, in addition to the native beta-Nb globular precipitates [14], the irradiation conducted below the monotectoid temperature leads to the precipitation of the supersaturated Nb, as predicted by the phase diagram.

EDX analyzes on extraction replica have measured a composition of about 60%wt Nb for these needle-shape nano-particles. This niobium content of 55–60% is similar to that of native beta-Nb particles irradiated at high fluences and is supposed to be the "equilibrium" composition of these particles under irradiation [15]. It should be pointed out herein that, based on the binary phase diagram [16,17], the equilibrium content of Nb in beta-Nb should be close to 91% at operating temperature. This suggests that the "equilibrium" composition under irradiation is not the thermodynamic equilibrium. Recently, these beta-Nb needle-shape nano-particles have been analyzed using synchrotron diffraction [11]. The diffraction peaks were consistent with BCC beta-Nb. Despite the difficulty for the T-XRD signal de-convolution and despite the possible elastic strain in these nano-precipitates that can modify the crystallographic parameters, the Nb content in these particles was evaluated from the measurement of the lattice parameter, using the Vegard's law, and was about 60% (lattice parameter a = 3.4150 A) up to 2 PWRs irradiation cycles. Therefore these nano-particles seem very similar to the native beta-Nb particles with the same crystallographic structure and the same composition under irradiation.

Sarce [18] explained, using the Maydet and Russel approach [19], the peculiar shape of these nano-precipitates by the assumed anisotropic diffusion of point defects. Nevertheless, Sarce [18] based its theoretical results on the hypothesis that beta-Nb particles are incoherent with the matrix while according to Turkin et al. [20], the beta-Nb particles are only partly coherent with the α-matrix. Turkin et al. [20] attributed the form of needles to the large interface energy. According to Turkin et al. [20], most of the interface of such a precipitate is coherent with the matrix, while the lattice misfit is accommodated at incoherent zones of the interface, which are small compared to the coherent ones.

The 3D geometry, the detailed interface structure and the Orientation Relationship (OR) of the beta-Nb nano-precipitates are topics of interest since these nano-precipitates may play a role on the post-irradiation mechanical properties of Zr-Nb alloys. Indeed, these nano-precipitates contribute to the remaining hardening observed after annealing out the irradiation damage, as pointed out in Refs. [21–23]. They also may play a role on the post-irradiation creep behavior, when irradiation damage annealing occurs, during the back-end cycles, such as transportation and dry storage of the fuel assembly.

In order to bring new insights on the beta-Nb nano-particles and their potential role on the post-irradiation mechanical behavior, a neutron irradiated sample made of Zr-1%Nb alloy, which has undergone first a heat treatment and then a creep test, has been studied. The beta-Nb nano-precipitates were analyzed using conventional TEM imaging and High Resolution Transmission Electron Microscopy (HRTEM).

2. Material and experimental details

The studied material is a Zr-1%Nb alloy, namely M5®, which is in a recrystallized metallurgical state [3]. This material is characterized by 6 μm size equiaxed grains with a strong crystallographic texture. The second phase particles are mainly 50 nm diameter spherical beta-Nb precipitates homogeneously dispersed throughout the grains.

The chemical composition (in wt%) of this commercial alloy is given in Table 1. This material has been irradiated as cladding tube in a PWR power plant at operating temperature of 623 K up to a fluence of 1.1×10^{26} n.m^{-2} (E > 1 MeV). After use, the cladding tube was cut, defueled and then several thermomechanical treatments were performed in order to study the behavior of the material. First a heat treatment was conducted at 723 K during 960 h, then, an internal pressure creep test was performed on the cladding at 673 K with an applied hoop stress equal to 130 MPa during 960 h. During these thermal treatment, there was a possible modification of the needle-like particle composition in order to reach the thermodynamic equilibrium composition. The results of the mechanical tests are not shown here, as the present paper focuses on the microstructure of the material. After testing, TEM thin foils were prepared in hot cell. Small tiles were cut out, mechanically-polished down to a thickness of 100 μm, then 3 mm disks were punched out, and jet-polished using Ethanol/Perchloric acid solution at 278 K.

2.1. TEM method

Conventional TEM was firstly conducted on a JEOL 2100 TEM operating at 200 kV. Two different imaging conditions were used: the nano-precipitates were observed in grains orientated with the electron beam in the basal plane, the basal plane being edge-on, using a diffraction vector along the c-axis (g = 0002). This

Table 1
Chemical composition of the Zr-1%Nb alloy.

Element	Nb	Fe	O	Zr
M5®	1.00	0.03	0.12	Balance