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Irradiation Effects on Fe Distributions in Zircaloy-2 and Zr-2.5Nb

Effets de l'irradiation sur la distribution du fer dans le Zircaloy-2 et dans du Zr-Nb 2,5%

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by

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EFFETS DE L'IRRADIATION SUR LA DISTRIBUTION DU FER DANS LE ZIRCALOY-2 ET DANS DU Zr-Nb 2,5 %

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RÉSUMÉ

L'irradiation du Zircaloy-2 (Zy) et du Zr-Nb 2,5 % (ZN) à gros grains avec des ions d'Ar de 1,5 MeV à une fluence de particules d'environ $10^{20}/m^2$ (env. 10 dpa) aux températures de 50, 300 et 420°C favorise la dissolution du Fe en phase α. Des analyses par microsonde électronique démontrent que les niveaux de Fe en phase α se situent entre 250 et 1 500 ppma comparativement à 70 ppma environ pour l'équivalent non irradié. Dans le ZN, les niveaux de Fe en phase β sont passés d'environ 6 000 à 3 500 ppma; ces résultats concordent quantitativement avec la perte de Fe en phase β après une irradiation par des neutrons dans des conditions normales de service. Des mesures effectuées sur le Zy ont démontré que les concentrations de Fe étaient supérieures à proximité de la surface de l'échantillon. Des données partielles sur la distribution du Ni dans le Zy indiquent pour le Ni un comportement similaire à celui du Fe.

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ABSTRACT

Irradiation of large-grained Zr-2.5Nb (ZN) and Zircaloy-2 (Zy) with 1.5 MeV Ar ions to a fluence of $\approx 10^{20}/m^2$ ($\equiv$ 10 dpa) at 50, 300 and 420°C leads to enhanced α-phase Fe dissolution. Electron microprobe analyses showed α-phase Fe levels of 250-1500 ppma, compared to equivalent non-irradiated state values of $\approx$ 70 ppma. In ZN the β-phase Fe levels fell from about 6000 to 3500 ppma: this result accords, qualitatively, with the loss of Fe from the β-phase following in-service neutron irradiation. Measurements on Zy showed that the Fe concentrations were higher near the specimen surfaces. Limited data for Ni distributions in Zy show similar (to Fe) behaviour.

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1. INTRODUCTION

Fe, at trace levels, or as an alloying component, controls self and substitutional diffusion in both α-Zr and the α-Zr based alloys, Zircaloy-2 and Zr-2.5Nb, henceforth referred to as Zy and ZN [1,2]. Fe also appears to be an active agent in breakaway growth in Zy [3] and in irradiation deformation of ZN [4]. Recent work on Fe in α-Zr, Zy and ZN (distribution, solubility and radiation effects) is described in references [5-9].

This work is the first quantitative study of the effect of irradiation on the level and distribution of Fe in the bulk α-phase of Zy and ZN; it follows an earlier equilibrium temperature dependence study [6]. Some data are also reported for Ni distributions in Zy.

2. EXPERIMENTAL

The alloys were prepared as described in reference [6]. Their compositions are, essentially, Zy: Zr + 0.56 O, 0.28 Fe, 0.23 Cr, and 0.09 Ni, and ZN: Zr + 2.5 Nb, 0.62 O, and 0.09 Fe (atom %, all concentrations are in "atomic units"). They had large, equiaxed grains, 40 μm for Zy and 10 μm for ZN. The specimens were approximately 4 x 5 x 1 mm^3. The surfaces for examination were prepared by grinding on metallographic papers down to 600 grit; they were then ground with 3 μm diamond paste on plate glass before being chemically polished for 10 to 20 s in 50 H_2O:40 HNO_3:10 HF, by volume. Reference measurements were made on a high-purity, Fe-free (< 1 ppm Fe) ZN alloy, HPZN.

Some specimens were mounted in place with a Ta mask, which shielded half the specimen surface from the 1.5 MeV Ar beam (as a reference); others were fully exposed to the beam. The alloys were irradiated for 3-4 h to fluences of ~ 1.0 x 10^{16} cm^{-2}, corresponding to ~ 10 to 30 displacements per atom (dpa). The beam homogeneity was better than ± 5% for an area of 50.0 mm^2. The residual pressure near the specimens was < 10^{-6} Pa during high-temperature irradiation.

Five specimens were irradiated at 420°C. Two were half-shielded and the beam was off during cooling, and three were fully exposed and the beam was left on during cooling. Two specimens were irradiated at 300°C and three at 50°C, all with the beam on during cooling. After irradiation, the specimen surfaces were clean and shiny.

Electron microprobe analyses (EMPA) of Fe in the α-phase of Zy and ZN were made at the grain centres. Typically, 5-10 measurements were made on different grains, the beam was rastered to cover patches (2 to 5 μm on edge), and as many as ten closely adjacent readings were recorded on the biggest grains. The strategy was to minimize residual carbon contamination of the analytical area. The usual operating voltage was 25 kV. A step-scan for Fe was also performed on the 420°C specimens.

3. RESULTS AND DISCUSSION

Table 1 lists the Fe levels measured by EMPA at 25 kV, and Table 2 (on page 4) lists depth distribution data for Fe and Ni in Zy. Unless specified otherwise, all the solute concentration data in Tables 1 and 2, and discussions thereof, refer to α-phase measurements.

Table 1. Fe Levels (ppm) in 1.5 MeV Ar Irradiated Zr Alloys

T°C	HP-ZN	ZN, beam-off* +Irr/Unirr.	Zy, beam-off Irr/Unirr.	Irradiated-Zy	Irradiated-ZN
420 ± 5	(α) 24 ± 40 (β) 12 ± 18	554/29	225/136	1400	1530 (β) 3517
300 ± 5				462	248
50 ± 5	(α) 20 ± 30 (β) 28 ± 23			362	48

*During cooling.

+"Irr" and "Unirr" refer to irradiated and unirradiated, respectively. The unirradiated state α-phase Fe reference levels for ZN and Zy are generally expected to be about 70 ppm; for the β-phase of ZN they are expected to be about 6000 ppm [6].

3.1 Table 1 Results

At 420°C, the Fe concentrations are highest for the beam-on during cooling, relatively high for the beam-off, and close to the reference values for the unirradiated samples; there has also been some loss of Fe from the β-phase. At 300°C, the Fe concentrations are much lower than the corresponding 420°C values, and at 50°C only Zy shows a radiation-induced increase in the Fe level.

"TRIM" calculations [10] show that the Ar profile peaks near 0.8 μm, with a tail to ≈ 1 μm, and that the damage profile peaks at about 0.6 μm. The damage distribution is non-uniform, with a relative intensity factor of 0.2 at the surface to a peak of 0.8 at about 0.6 μm.

3.1.1 420°C Data

3.1.1.1 Cooling: beam-on

The high Fe levels of the irradiated volume (IRV) of the α-phase of ZN imply that, in addition to a β → α Fe redistribution in the IRV (the β-phase Fe has fallen from ≈ 6000 to 3500 ppm), Fe has also migrated into the IRV from below. Tracer diffusion data [11] for Zy

and ZN indicate that the diffusion coefficient of Fe at 420°C should be D(Fe) ≈ 3 x 10^{-15} m^2/s; coupled with the irradiation time, this gives a mean diffusion distance, $(Dt)^{0.5}$ ≈ 6 μm, sufficient to account for the observed Fe build-up.

In Zy, the enhanced IRV α-phase Fe levels could have arisen solely from a redistribution of Fe (from grain-boundary precipitates) in the IRV. However, the limited Fe diffusion distance suggests that this would require radiation-enhanced diffusion (RED) of Fe. Possibly, both RED and Fe diffusion were occurring to the IRV from below.

The high Fe levels in ZN and Zy here, compared to the beam-off cooling data, indicate stabilization of Fe in the IRV by continuously generated defects, and, conversely, a loss of Fe and defects from the IRV with the beam-off. It seems likely that the "at-temperature" Fe levels would have been higher than those listed in Table 1.

3.1.1.2 Cooling: beam-off

In ZN and Zy, the Fe concentration falls by about 3-6 times in a few minutes. This fact leads to inferences, as described below.

Firstly, the excess Fe in the IRV is not in a stable second-phase form; it is, evidently, mostly mobile (e.g., point defects). This may be considered to be consistent with the general absence of second-phase, Fe-rich precipitates in the Fe-saturated α-matrix of both ZN and dilute, binary Zr(Fe) alloys -- a result that may reflect second-phase nucleation difficulties [5,7].

Secondly, the excess Fe does not aggregate (principally) at the surface, as is customary of supersaturated Fe in single-crystal dilute Zr(Fe) alloys [5,7,12]. Possibly the alloy surfaces, under the present conditions, are "blocked" to the easy effusion of Fe. Since ZN is metastable, the surface of the alloy may have a composition different from that of the matrix (e.g., Nb enrichment). Proton irradiation of Zy at 90-200°C to 1-2 dpa has been shown to lead to surface, or near-surface, Sn enrichment [13].

Thirdly, since $(Dt)^{0.5}$ < 1.0 μm, for the cooling period, the main loss of Fe from the IRV is probably by diffusion into the underlying matrix.

3.1.2 300°C Data

The probable bulk Fe diffusion distance into ZN and Zy for the irradiation time is (Dt)0.5 ≈ 0.06 μ [11]. This suggests that enhanced IRV Fe levels are associated with fast Fe transport processes, such as RED or grain boundary, surface and dislocation diffusion. In both alloys, the Fe levels are such that the RED in the IRV could be the sole transport mechanism; an effective D(Fe) ≈ 5 x 10^{-16} m^2/s seems to be needed.

3.1.3 50°C Data

There is a significant IRV enhancement of Fe in Zy, but essentially none in ZN. There is evidently still some effective Fe transport mechanism at work in Zy; RED seems most likely. The relatively small difference in the IRV Fe enhancement in Zy for the 300 and 50°C conditions suggests an effectively low activation energy process, unlike the ZN case. Positron annihilation spectroscopy of the recovery of low-temperature irradiated Zy and ZN [14] suggests that at 50°C Fe atoms are clustered with irradiation defects in ZN, but not in Zy. Possibly such clustering limits long-range migration of Fe.

3.2 Table 2 (420°C)

Table 2 shows that Ni, like Fe, in the IRV of Zy is enhanced and that both the Fe and Ni distributions are skewed towards the surface; also, their distributions do not quite follow the damage distribution.

Table 2. Fe and Ni Distributions vs. Depth in α-phase of Zircaloy-2 Irradiated at 420°C

Voltage (kV)	10	15	25
Fe (ppm)	2024	1584	1168
Ni* (ppm)	943	589	380
Depth+ (μm)	0.21	0.63	1.65

+ The excitation depth defined by $3/2\alpha$, where α; see reference [6]. *The unirradiated state α-phase Ni reference level is 180 ppm.

3.3 Phenomenology

The irradiation-driven dissolution of Fe into the α-phases of ZN and Zy can be understood, in principle, in terms of radiation-induced defects and Fe-defect interactions. Irradiation produces vacancies and interstitials, and agglomerations of these defects (e.g., loops). It has been postulated, on the basis of α-Zr self-diffusion and positron annihilation investigations, that Fe-vacancy complexes in α-Zr are very strongly bound (≈ 1.4 eV), and that they have very low migration energies [14,15]. The probability of substitutional Fe/SIA site interchange has been predicted [16], and there is some evidence for the accrual of Fe atoms at dislocations in α-Zr [8,17]; this may be expected on general grounds.

Results of lattice location studies of Fe in single crystals of α-Zr, and of β-stabilized Zr-19%Nb-1%Fe, show that Fe is substitutional in the β-phase and non-substitutional in the α-phase [18]. In the IRV of the β-phase, SIA's will tend to displace Fe, and the resulting Fe interstitials, unstable defects, will annihilate vacancies and/or migrate to the α-β interface;

from the interface they may migrate into the α-phase as strongly bound and mobile complexes with vacancies. Since Fe is substitutional in second-phase particles in Zy, it is probable that a similar α-phase enrichment process may occur.

The diffusion and defect behaviour of Ni in Zr is very much like that of Fe [1], and so it may be anticipated that its irradiation behaviour will be like that of Fe.

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