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Letter to the Editors

Effect of molybdenum on electron radiation damage of Zr-base alloys

J.H. Lee [a], S.K. Hwang [a,b,*], K. Yasuda [c], C. Kinoshita [c]

[a] *Department of Metallurgical Engineering, School of Materials Science and Engineering, Inha University, Inchon 402-741, South Korea*
[b] *Center for Advanced Aerospace Materials, School of Materials Science and Engineering, Inha University, Inchon 402-741, South Korea*
[c] *Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, 36, Fukuoka 812-8581, Japan*

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Abstract

The effect of Mo on the radiation damage of the Zr–1Nb–1Sn–0.1Fe alloy was studied by in situ electron beam irradiation using a high-voltage electron microscope (HVEM) operated at 1 MeV equipped with a heating device. Regardless of the Mo content, the nucleation rate as well as the growth rate of radiation defects increased with irradiation temperature. Addition of 0.5% Mo decreased the initial nucleation rate and suppressed the growth rate of radiation defects in the alloy at 300°C. Extended annealing heat treatment at 650°C further increased the radiation resistance of the Mo-containing alloy.

1. Introduction

Zr-base alloys for nuclear applications are subject to neutron irradiation which results in growth and irradiation creep of hardware components. Over the past years, alloy design efforts [1–7] have identified a composition based on Zr–1Nb–1Sn–Fe as a practical solution for fuel claddings with improved corrosion resistance and yield strength. An evaluation of this type of alloy under irradiation environment, however, has not been fully documented. More recently, the modification of this composition with Mo-additions was attempted to further increase the yield strength by refining the microstructure [8–12]. It was also found that Mo-additions stabilized the microstructure against coarsening during high-temperature exposure. This led to an investigation of the effect of Mo-additions on the resistance of the alloy to irradiation. As a first step in this research, the present work deals with the response of the material to electron irradiation with a particular interest in the role of Mo as a microstructure stabilizer.

2. Materials and experimental procedure

Button ingots of two different chemical compositions were prepared with a plasma arc re-melting apparatus: Zr–1%Nb–1%Sn–0.1%Fe and Zr–1%Nb–1%Sn–0.1%Fe–0.5%Mo in weight pct. The ingots were forged, β heat-treated, hot rolled, β-annealed and cold rolled 75% into plates. Details of materials processing can be found elsewhere [10,12]. The final annealing heat treatment was conducted at 600°C/16 h for both alloys. For Zr–1%Nb–1%Sn–0.1%Fe–0.5%Mo alloy, additional samples were prepared with a heat treatment at 650°C/32 h. The electron microscope used for irradiation and examination was a JEM-1000 that was operated under the accelerating voltage of 1 MeV equipped with a heating device. The irradiation was conducted at room temperature, 200°C and 300°C, respectively, with the electron fluxes of 2×10^{19} e/cm^2 s at 200°C and 3.3×10^{19} e/cm^2 s at 300°C at a magnification of 50 000. Samples were exposed up to a total of 40 min inside the TEM sample specimen holder, which would result in approximately 0.7×10^{-3} dpa/s and 1.2×10^{-3} dpa/s at 200°C and 300°C, respectively [13,14].

* Corresponding author. Tel.: +82-32 860 7537; fax: +82-32 862 5546.
E-mail address: skhwang@inha.ac.kr (S.K. Hwang).

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3. Results

In the as-received condition prior to irradiation, Zr–1%Nb–1%Sn–0.1%Fe samples showed a typical recrystallization annealed microstructure of low dislocation density whereas Zr–1%Nb–1%Sn–0.1%Fe–0.5%Mo samples showed a higher density of dislocation in either conditions of heat treatment, 600°C/16 h or 650°C/32 h. In the Zr–1%Nb–1%Sn–0.1%Fe alloy, second-phase particles, mostly $(Zr, Nb)_2Fe$ or β-Zr, were also found, which ranged from 10 to 150 nm in diameter. With the addition of 0.5% Mo, the β-Zr phase tended to become β-Nb containing high Mo, indicating that a large portion of Mo partitioned in the precipitates.

Irradiation at room temperature did not result in any significant change in the microstructure. Therefore, subsequent irradiation experiments were conducted at 200°C and 300°C.

Since the TEM data presented here were obtained from the in situ irradiation of thin foils, there might have been a surface effect. As noted by Buckley et al. [15], being a potent sink site, the surface can cause significant annealing-out of point defects. Oxidation and accumulation of the alloying elements at the specimen surface multiply the complexity of the balance between vacancies and self-interstitial atoms. To minimize the surface effect, we fixed the areas of TEM observation at approximately the same thickness among the specimen, which was greater than 100 nm.

During the elevated temperature irradiation, defects initially appeared as black dots of approximately 10 nm in diameter in the nucleation stage and then they grew in size with time up to about 40 nm in diameter. Typical morphology and distribution characteristics of the defects with irradiation time are shown in Fig. 1. Individual defects grew in size either by themselves or by coalescence of adjacent defects.

Since the defects were in an early stage of growth under low dpa we have not attempted to analyze the characteristics of the dislocation loops, whether interstitial type or vacancy-type. In general, the characteristics of the loops vary sensitively with irradiation temperature and fluence. In an earlier electron irradiation study of Zircaloy, Gelles and Harbottle [16] concluded that the dislocation loops produced by 1 MeV irradiation were mostly of the interstitial type. Later, Griffiths et al. [17] reported vacancy-type loops coexisting with the interstitial type loops in Zr irradiated under

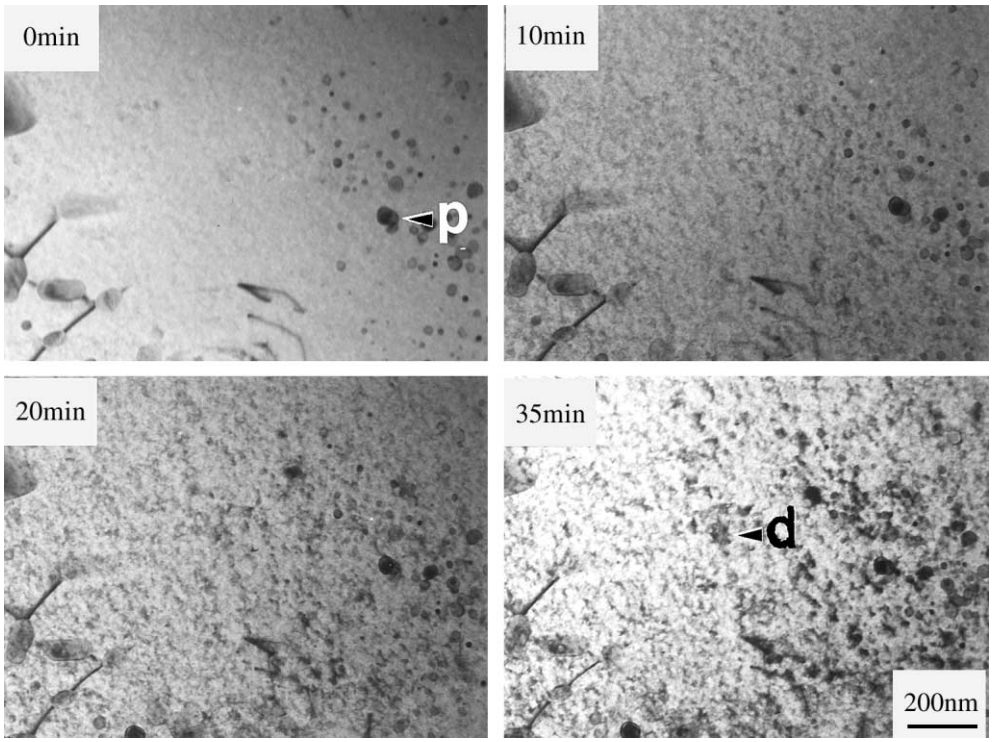

Fig. 1. Development of electron radiation defects in the Zr–1%Nb–1%Sn–0.1%Fe alloy heat-treated at 600°C/16 h and irradiated at 200°C at a flux of 2×10^{19} e/cm^2 s for the time span as indicated. Dot-like radiation defects (marked as 'd') grew to approximately 37 nm in diameter after 35 min exposure. Prior to irradiation (0 min exposure), the sample contained second-phase particles (marked as 'p'), presumably β-Zr or intermetallic compounds based on $(Zr, Nb)_2Fe$, which should not be confused with the radiation defects.

similar conditions. According to a previous study using the identical equipment and mostly the same irradiation flux to those used in the present work, Nakamichi et al. [18] found that the dislocation loops were of only interstitial type in commercial purity Zircaloy-2, Zircaloy-4 and Zircaloy-2 containing high Fe and Ni. This conclusion may also be applicable to the present case because the appearance of the dislocation loops in the two works is very similar.

At fixed temperature, radiation defects increased with time in number as well as in size. With increasing irradiation time, the areal number density of defects increased abruptly and then decreased to a saturation value or decreased continuously, depending on the alloy composition and heat treatment given. Fig. 2 shows the variation in the areal number density of defects with irradiation time at 200°C and 300°C. Except for Zr–1%Nb–1%Sn–0.1%Fe–0.5%Mo alloy heat treated at 650°C/32 h, all the samples showed an initial increase in the number of defects.

Within an identical composition, the number density of defects decreased with the annealing time and temperature of samples. Comparison of the data for Zr–1%Nb–1%Sn–0.1%Fe–0.5%Mo alloy annealed at 600°C/16 h and at 650°C/32 h in Fig. 2 confirms this observation. The longer annealing time and higher annealing temperature resulted in a smaller number of defects during irradiation.

Radiation defects grew faster under higher temperature exposure. This is evident from comparing the results of the Zr–1%Nb–1%Sn–0.1%Fe alloy irradiated at 200°C and 300°C. In this alloy, particularly at 300°C, the initial increase in the defect number density was

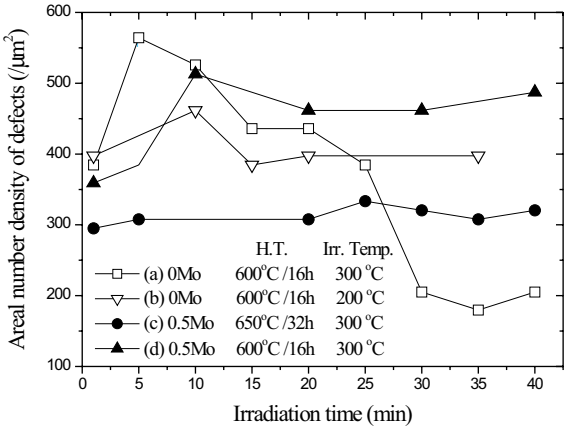

Fig. 2. Variation in areal number density of defects in two different Zr-base alloys with electron irradiation time at elevated temperatures. Note the substantial decrease in the areal number density of defects in the Zr–1%Nb–1%Sn–0.1%Fe alloy in the later stage of irradiation at 300°C, which is caused by coarsening and recombination.

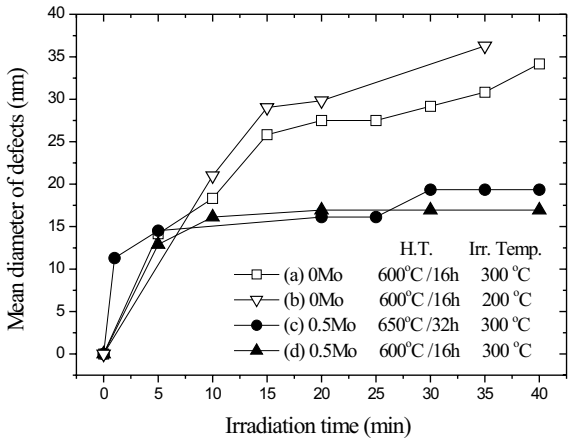

Fig. 3. Growth of defects in two different Zr-base alloys with electron irradiation time at elevated temperatures. Note the effect of Mo addition in suppressing the growth rate of defects.

followed by a substantial decrement in the later stage – indication of defect coalescence. Due to the low flux, the defect number density was nearly constant at 200°C although there was a small increase in the early stage.

Addition of Mo suppressed the initial increase rate of the defect number density as can be ascertained by comparing the (a) and (d) conditions in Fig. 2. Also the growth rate of the alloy containing Mo was remarkably lower than the other as shown in Fig. 3. In the Mo-free alloy, irradiation defects continued to grow upon extended exposure.

4. Discussion

From the dark TEM contrast of the defects, it is surmised that the defects are interstitial type displaced atoms. The initial increase followed by a decrease of the number density of defects as shown in Fig. 2 agrees with the trend predicted by theory [15,17].

The effect of Mo in suppressing the growth rate of radiation defect loops may be interpreted in terms of the sink sites and the dislocation structure. Addition of Mo in the present alloy system increases the number of second-phase particles containing Mo, of which the interfaces with the matrix act as the recombination centers for self-interstitial atoms and vacancies generated by irradiation. Mo atoms present in the matrix solid solution stabilize dislocation structures, retarding the climb rate of the loops.

A perspective view of the Mo effect is the retardation of the diffusion-controlled process in Zr-alloys. In previous work [8–12], we reported that Mo addition refined the microstructure and strengthened the Zr-base alloys. Grain growth was suppressed during recrystallization

annealing as well as during exposure to the high-temperature β phase field by Mo addition. Dislocation structures were persistent during recrystallization annealing heat treatment. The Widmanstätten type lamellar structure was also persistent during the β heat treatment. All these facts point to a retardation of the diffusion rate. Since the formation and recombination of radiation defects are essentially controlled by atomic diffusion their kinetics will also be suppressed by Mo addition.

5. Conclusions

The present work showed that Mo addition enhanced the radiation resistance of a Zr-base alloy during electron beam exposure. Although the damaging processes are different, Frenkel defects vs. cascades and subcascades, respectively, during electron irradiation and neutron irradiation this result hints at a possible method of increasing the neutron radiation resistance of Zr-base alloys. Combined with the grain refining and strengthening effect also Mo may be considered as a potential alloying addition candidate for Zr-base alloys for nuclear core materials applications.

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