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ARTICLE

Defects and Microstructural Evolution of Cold-rolled Pure Zirconium Under Isochronal Annealing Conditions

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Abstract: The defects and microstructural evolution of cold-rolled pure zirconium with different deformation reduction under isochronal annealing condition were investigated using positron annihilation lifetime (PAL) and transmission electron microscopy (TEM). The results show cold-rolling deformation introduces dislocations and vacancies with high density into the pure zirconium; the mean lifetime increases with increasing the amount of deformation up to 10% and then saturates with increasing cold-rolling reduction. Furthermore, vacancy clusters in the cold-rolled pure zirconium do not form, and they do not grow even under the isochronal annealing conditions of 298~898 K. The vacancy and dislocation densities of the cold-rolled pure zirconium decrease with increasing the annealing temperature, and recovery almost finishes at 873 K.

Key words: positron annihilation lifetime; pure zirconium; defects; isochronal annealing

Zirconium alloys are extensively used as nuclear reactor materials such as guide tubes and fuel cladding because of their low thermal neutron absorption cross-section and excellent corrosion-resistant properties in high-temperature and high-pressure water compared to other commercial structure materials[1-4]. In the reactor core, zirconium alloys have to endure to high-energy neutron irradiation, probably causing radiation-induced defects, hardening, creep, growth and amorphization[1]. Namely, the irradiation effects originating from the evolution of points defects and defect clusters, accumulation and dissolution, finally result in degradation of physical and mechanical properties of materials. It is well known that the evolution behavior of the irradiation defects in metallic alloys is almost controlled by atomic scale diffusion[1-4]. In particular, the formation of second phase precipitates and the amount of additional alloying elements are affected by the diffusion of vacancies with the local configuration. In order to successfully assess and predict material performance for long periods of time exposing in irradiation environment, it is essential to understand the basic formation mechanisms of defects and microstructural evolution of the metallic materials.

There have been a certain amount of studies involving irradiation damage and microstructural evolution of zirconium and its alloys under various irradiation which were simulation of in-pile neutron irradiation damage[5-10]. It is well known that the energetic particles bombard the material triggering off cascade collisions, point defects, dislocation loop. Through a large number of experimental and simulation studies, the formation mechanism of the dislocation loops and their influence on mechanical properties of zirconium and its alloy have been certainly understood for the development and improvement of advanced materials tolerant of high irradiation dose. However, there are few studies on intrinsic defects evolution behavior in cold worked pure zirconium, which is conducive to further assess and predict zirconium alloy performance for long periods of time under irradiation.

In the case of studying quantificationally defect structure, it is still a challenging work even if several matured analytical/microscopic techniques are available. Scanning electron microscopy (SEM) is only used to observe and analyze the microstructure of the surface for materials. And

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transmission electron microscopy (TEM) is a feasible tool to characterize crystal defects and bubbles by irradiation, such as line and interfacial defects, but it is also ineffective in overall defect characterization and lack of statistical function[11]. X-ray diffractometry is based on diffraction peaks to identify dislocation density, texture, micro-stress and lattice strain. Positron annihilation spectroscopy (PAS), which is pretty sensitive to detect different types of defects due to their long diffusion length and their attraction to atomic-size defects, can be widely used for characterizing vacancies and interfaces in the materials[11-15].

The present paper aims to investigate the introduced defects evolution including vacancies, dislocations in cold worked pure zirconium using positron annihilation spectroscopy (PAS) and transmission electron microscopy (TEM) during isochronal annealing. The pure zirconium was chosen to obtain ideal results to avoid the influence of alloying elements on positron annihilation.

1 Experiment

The samples used in the present work were prepared from a 100 μm thickness hot rolled zirconium sheet of purity of 99.3%. From the sheet, rectangular plate (50 mm length×20 mm width×100 μm thickness) samples were made. The plates were annealed at 873 K for 2 h in vacuum at lower than 1 × 10^{-4} Pa. Fig.1 shows the microstructure of annealed pure zirconium; the microstructure only contains single α phase and there is not dislocation defects observed in the matrix. Then, they were cold rolled to reduce the thickness by 5%, 10%, 20% and 40% at ambient temperature. The cold rolled plates were punched to 5 and 3 mm in diameter and then chemically polished. The former samples were for PAS measurement, and latter for TEM observation.

Samples with 10% and 20% reduction in thickness were chosen for isochronal annealing experiments which were performed at interval of 50 K from 348 to 848 K for 60 min. Positron annihilation lifetimes tests were carried out using a fast-fast time spectrometer with the Hamamatsu photomultiplier tubes H3378 and the BaF2 scintillators. The time resolution of the system in the present work was around 190 ps in full width at half maximum (FWHM). The resolution and Positronfit programs were used to analyze the positron lifetime spectra. Each spectrum was accumulated to a total of approximately 1.2×106 counts. All of measurement temperature of positron annihilation lifetime was at ambient temperature. Samples for TEM analysis were electropolished by a twin jet to reduce thickness to about 100 nm at a temperature less than 253 K in an electrolyte mixture containing 90 vol% methanol and 10 vol% perchloric acid. The voltage was kept constant at 14 V during electropolishing. Then these specimens were observed using JEM2010 at 200 kV to investigate the microstructural features and recovery of defect structures of the alloy.

2 Results and Discussion

2.1 Positron lifetime analysis

Fig.2 shows the positron annihilation lifetimes and intensity of long lifetime of the pure zirconium as a consequence of cold-rolling reduction from 0% to 40%. It can be noticed that the positron lifetime spectra contain only one component for the deformation reduction less than 10%, while the spectra for the cold-rolled samples with 10%, 20% and 40% reduction are well decomposed into two components (short lifetime=τ_1, long lifetime=τ_2). It is well known that the short lifetime τ_1 presents the lifetime for combined effects of positrons annihilating in the bulk and those with free Bloch state residence time, while long lifetime τ_2 indicates the lifetime of trapped positrons in vacancy-type defects or micro-defects[3,16]. Moreover, the positron annihilation lifetime of the pure zirconium after isothermal annealing at 873 K for 2 h is approximately 161.2 ±0.3 ps, which is in agreement with the data reported in the paper as the bulk lifetime for Zr[11]. The mean lifetime increases after the cold-rolling reduction by about 5%, and

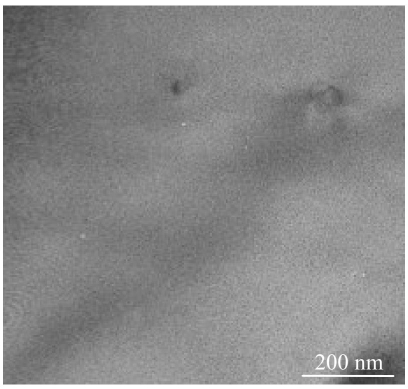

Fig.1 Microstructure of as-received pure zirconium annealed at 873 K for 2 h

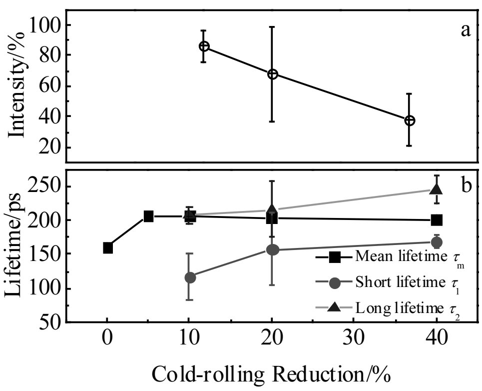

Fig.2 Intensity of long lifetime (a) and positron lifetime (b) as a function of the cold-rolling reduction for pure zirconium

then it is almost constant with increasing deformation up to 40% as shown in Fig.2. However, PALS spectrum could be analyzed in two components when the amount of deformation increases to 10%. The observed τ_1 for the cold-rolled pure zirconium is shorter than that for the bulk lifetime (161 ps), indicating that positrons are primarily trapped at one type of defect. Additionally, it is clear that the long lifetime τ_2 of the cold-rolled pure zirconium increases with increasing the cold-rolling reduction. The value of the long lifetime more and more tends to 252 ps for a positron trapped at the monovacancy in zirconium[11]. The results indicate that, as a consequence of a cold deformation for cold-rolled pure zirconium, dislocations and vacancies occur, and the positrons are trapped by dislocation- vacancies complexes.

Fig.3 shows the positron annihilation lifetime of the pure zirconium with cold-rolling reduction of 10% as a function of annealing temperatures from 298 K to 848 K. It can be seen that most of positron lifetime spectra are well decomposed into two components. The mean lifetime and long lifetime increase slightly at the initial stage of annealing from 298 K to 398 K. Then, the mean lifetime decreases gradually to ~161 ps (bulk lifetime) with increasing the annealing temperatures.

All of the short lifetime (τ_1) observed are lower than 161 ps, the bulk lifetime of well annealed at 873 K for 2 h. These results indicate that the positrons are primarily trapped at the defects induced by 10% cold-rolling deformation. In terms of the long lifetime, all of the values of the long lifetime are lower than 252 ps, implying the positron trapping at deformation-induced defects such as dislocation-vacancies complexes, other than large sized vacancy clusters. Usually, the vacancy clusters induced by deformation or irradiation grow during annealing even in bcc metals that present good irradiation resistance[17]. In the present study, vacancies do not obviously aggregate during annealing. This suggests that the irradiation resistance of zirconium is good.

Fig.4 shows the positron annihilation lifetime of the pure

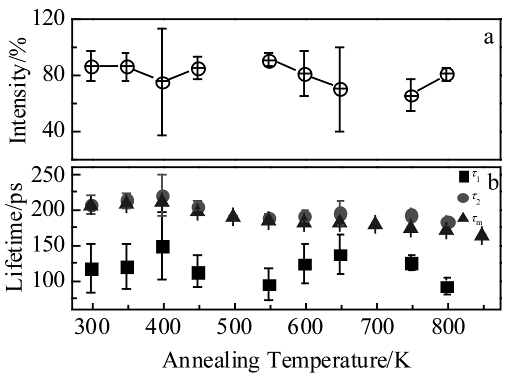

Fig.3 Intensity of the long lifetime component (a) and short lifetime, mean lifetime, long lifetime of pure zirconium cold-rolled with 10% reduction during isochronal annealing (b)

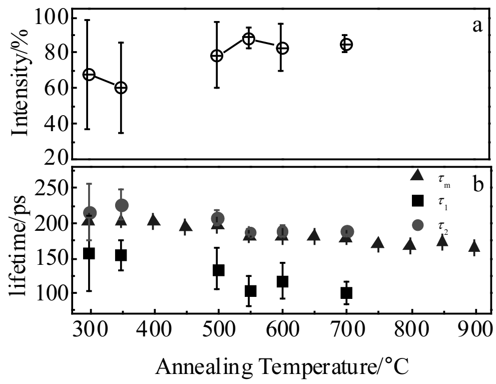

Fig.4 Intensity of the long lifetime component (a) and short lifetime, mean lifetime, long lifetime of pure zirconium cold-rolled with 20% reduction during isochronal annealing (b)

zirconium with a cold-rolling reduction of 20% as a function of annealing temperature from 298 K to 848 K. It is clear that, the change in the mean lifetime is almost similar to that of 10% except for initial stage of annealing from 298 K to 398 K. Only few of the positron annihilation spectra could be decomposed into two components during annealing. This means that the proportion of defects disappearing is small during annealing.

2.2 Microstructure analysis during annealing

Fig.5 shows TEM images of cold-rolled pure zirconium with 10%, 20% and 40% reduction. It is observed that a large amount of dislocation tangles and loops are produced. The density of dislocation increases noticeably with increasing the deformation amount by cold rolling. Since the migration energy of vacancy is 0.7 eV in pure zirconium [18], the vacancies are mobile at room temperature. They are trapped by dislocations and form dislocation-vacancies complexes. Moreover, the dislocations tend to accumulate at local region in the pure zirconium cold rolled with 10% and 20% reduction, as shown in Fig.5a and 5b. While dislocations remarkably uniformly distribute in the matrix of the alloy cold rolled with 40% reduction (in Fig.5c). For the pure zirconium, because of the random crystallographic orientations of the numerous grains, the dislocation motion does not simultaneously occur in the all of grains under applied stress[19]. As a consequence, the dislocation motion occurs in the grains that have the most favorable orientation when the cold-rolling reduction is lower for the pure zirconium, leading to ununiform distribution of the dislocation.

Fig.6 shows TEM images of cold-rolled pure zirconium with 10% and 20% reduction after isochronal annealing at 473 and 673 K for 60 min. Dislocation densities decrease with increasing annealing temperatures in both cases. The decrease in dislocation density causes the decrease in positron lifetime. Compared with annealing at 473 K, the dislocation net-work and cell structure have almost disappeared and most

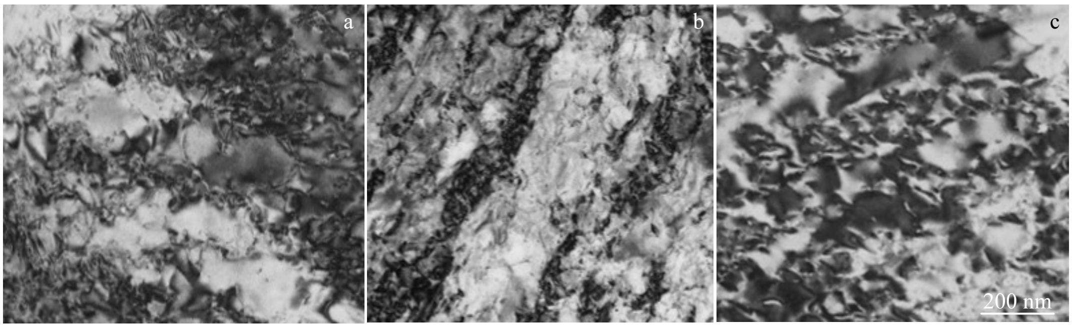

Fig.5 Microstructures of cold-rolled pure zirconium with different deformation reductions: (a) 10%, (b) 20%, and (c) 40%

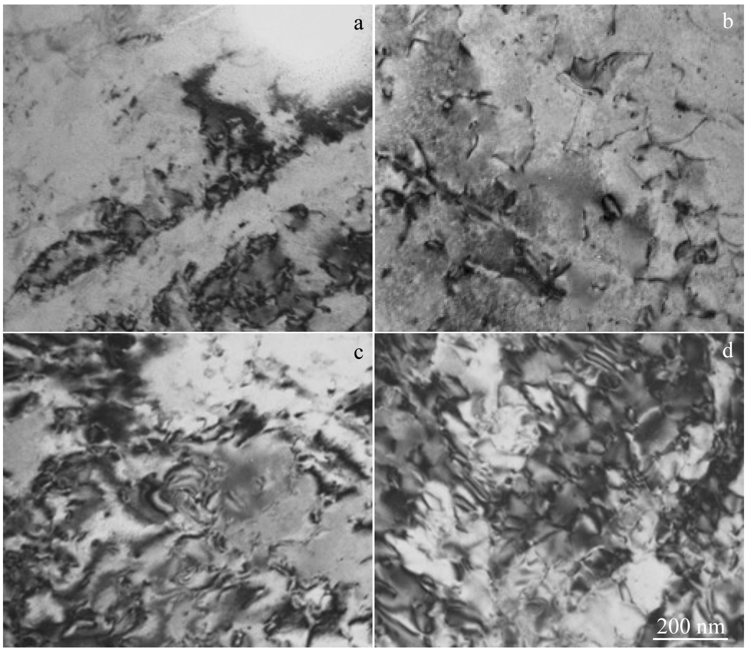

Fig.6 Microstructures of the pure Zr cold-rolled with 10% (a, b) and 20% (c, d) reduction after isochronal annealing at different temperatures for 60 min: (a, c) 473 K and (b, d) 673 K

dislocations recover in the deformed alloy annealed at 673 K, resulting in the further decrease in the lifetime. It is different that the density of dislocation in the alloy cold-rolled with 20% reduction is more than that of 10% reduction under the same annealing temperature conditions. Thereafter, the mean lifetimes of the alloy cold-rolled with 20% and 10% reduction are almost the same. This suggests that the density of defects induced by 10% reduction in zirconium exceeds the resolution of PAL method.

3 Conclusions

1) Dislocations and vacancies are produced in the pure zirconium by cold-rolling. Dislocation-vacancies complexes are trapping sites of positrons. The mean lifetime increases with increasing the deformation up to 10% and then saturates. The dislocation density, on the other hand, increases with increasing the deformation amount.

2) Although vacancies form by cold-rolling, but vacancy clusters do not form during annealing. This indicates that it is difficult to form vacancy clusters in pure zirconium.

3) Positron mean lifetimes of zirconium with 10% and 20% reductions decrease with increasing the annealing temperature. This is caused by the decrease in dislocation density during annealing.

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冷轧纯锆在等时退火条件下的缺陷和组织演化

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摘　要：通过正电子湮没寿命（PAL）和透射电子显微镜（TEM）研究了不同程度冷轧纯锆在等时退火条件下的缺陷和显微组织演化行为。研究结果表明：纯锆经过冷轧变形产生高密度的位错和空位，随着冷轧变形量增加到 10%，正电子的平均湮没寿命逐渐增加，变形量进一步增大，正电子的平均寿命趋于饱和。在温度范围 298~898 K 的等时退火条件下，冷轧纯锆中的空位型缺陷并没有聚集形成空位簇。随着退火温度增加，冷轧纯锆中的空位和位错密度逐渐减小，在退火温度为 873 K 时回复基本完成。

关键词：正电子湮没寿命；纯锆；缺陷；等时退火

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