Surface & Coatings Technology 284 (2015) 63–68

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Microstructure changes in Zr–1Nb alloy after pulsed electron beam surface modification and hydrogenation

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ARTICLE INFO

Article history:
Received 7 April 2015
Revised 9 July 2015
Accepted in revised form 9 July 2015
Available online 20 August 2015

Keywords:
Zirconium alloy
Low energy high current pulsed electron beam
Hydrogenation
Defect structure

ABSTRACT

In this paper the results of experimental study of microstructure changes in Zr–1Nb alloy after low energy high current pulsed electron beam surface modification and hydrogenation are discussed. Surface treatment was carried out with energy density equal from 5 to 25 J/cm^2 and impulses number equal from 1 to 5. Subsequent hydrogenation was carried out at temperature equal to 350 °C until reaching the hydrogen concentration of 0.05 wt.%. The structure was analyzed by X-ray diffraction, transmission electron microscopy and by means of electron–positron techniques.

1. Introduction

The investigation of different surface treatment effects on the hydrogen diffusion and absorption characteristics in metals and alloys is of paramount importance for many industries such as nuclear and hydrogen power, oil and gas industry and other areas dealing with structures operating in hydrogen isotopes environment and any hydrogen-containing media [1–3]. Primarily such studies present interest for the development of hydrogen storage materials. Secondly, the information about these characteristics is decisive for choosing the methods to improve materials resistance to hydrogen. In particular, these studies are relevant to zirconium alloys behavior in harsh effects of temperature, radiation and corrosive environment [4,5]. The necessity of nuclear reactors life extension makes it necessary to solve the problems of hydrogenation level reduction for zirconium components of reactor core. The improvement of the materials mechanical properties is important as well since the zirconium components stay longer in contact with water coolant. Zirconium materials are subject to hydrogenation during operation and hydrogen penetration is inevitable due to technical service conditions [6,7]. Corrosion interaction of zirconium with core coolant, hydrogen presented under the fuel cladding and released from the fuel during operation are the sources of hydrogen accumulation in the zirconium components of nuclear reactor core. Molecular hydrogen dissociates on the cladding surface and then atomic hydrogen diffuses into cladding [8].

Metal catalytic activity and hydrogen permeability can be changed in any direction by changing structural and defect conditions of the metal surface layers. In this regard surface modification by any conventional method and the investigation of hydrogen influence on material microstructure are promising [9–12]. Treatment by low energy high current pulsed electron beam (LEHCPEB) is an effective method for metals and alloys properties modification [12–18]. Fast heating and subsequent cooling, propagation of shock waves, vacancies and impurities migration due to radiation and temperature gradient lead to significant change in the structural-phase and defect states in the surface layers as well as to modification of the structure dependent material properties. Thus in [3] it is shown that the rapid heating and cooling changes the surface structure, material quenching takes place and large amount of vacancy type defects is formed. In the article [4] the conducted investigation of beam fluence on defect structure of metals is discussed. It was found that increase of the beam fluence entails decrease in the concentration of vacancy-type defects (vacancies, divacancies), which the authors relate to the coagulation of vacancies and the formation of larger defects consisting of 3, 4 or more vacancies. In [4–8] the phase transformation of materials after irradiation by LEHCPEB was studied. Fused areas were observed after irradiation. Further in all the grains the traces of plastic deformation were discovered, which appeared to be the result of thermal stresses. Changes in the grain and dislocation structure of the material have been found. These changes are attributed by the authors to the rapid heating of the surface layers to the melting temperature and above as well as to the influence of stress waves. In [9] it was shown that the effect of thermoelastic stress field during LEHCPEB irradiation causes manifestation of the long-range stress fields, and leads to bending-torsion of

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http://dx.doi.org/10.1016/j.surfcoat.2015.07.082
0257-8972/

the crystal lattice and the appearance of extinction contours. Further the authors conclude that the change in the phase composition of the heat affected zone leads to the change in the state of the Cottrell sphere and dislocation cores [19]. The microstructure and defect structure changes in Zr–1Nb alloy after modification by LEHCPEB as well as hydrogenation were studied in this work.

2. Experimental procedures

The zirconium alloy Zr–1Nb samples with dimensions 20 × 20 × 0.7 mm were prepared for research. The samples surface was mechanically grinded and polished. The roughness of the surface before treating was ~0.9 μm and after treating was ~0.05 μm.

The sample was irradiated by LEHCPEB using "Solo" device in Institute of High Current Electronics of Siberian Branch of the Russian Academy Of Sciences. The both sides of the sample were treated with the energy density of 5–25 J/cm^2. Every sample was irradiated by 1–3 pulses with duration of 50 μs. Hydrogenation was conducted using automated complex Gas Reaction Controller [20,21] at temperature 350 °C and constant pressure 2 atm. during different time for different parameters of irradiation [11] for concentration 500 ppm. Hydrogen concentration was determined by melting in argon atmosphere using hydrogen analyzer RHEN602 by LECO. The analysis of alloy surface structure was performed by transmission electron microscopy. Structure and phase composition was analyzed using Shimadzu XRD 7000S diffractometer.

Investigation of positron lifetime (PL) in the material and Doppler broadening (DB) shift of annihilation photons were performed for studying the defect structure evolution of Zr–1Nb alloy after irradiation by LEHCPEB and hydrogenation. The special complex for defect studying by positron spectroscopy was used, it was developed at the Department of General Physics in National Research Tomsk Polytechnic University [22–24]. Positron lifetime and Doppler broadening spectra were collected simultaneously and the positron source was represented by a ^{44}Ti isotope with maximum positron energy of 1.47 MeV. PL spectra with $5 \cdot 10^6$ counts each were collected for every sample. Spectra were fitted using LT10 software [25] with the help of multi exponential model [26]. Two components τ_1 and τ_2 and two intensities I_1 and I_2 as well as average positron lifetime $\tau_{avg} = \tau_1 \cdot I_1 + \tau_2 \cdot I_2$ were analyzed. DB spectra were acquired by collecting $2.5 \cdot 10^6$ counts and analyzed using SP software package [27]. The line-shape parameters S and W were also evaluated using the aforementioned software [28]. The S parameter is defined as the area of the central low-momentum part of the annihilation peak divided by the net peak area. The W parameter is taken as the area of the high-momentum region far from the center of the peak divided by the net peak area. Thus S parameter is associated with positron annihilation with valence electrons and W parameter — with positron annihilation with core electrons. R parameter which is dependence S = f(W) was analyzed [29,30]. The average depth of positron penetration was determined by the method proposed in [31] and it is equal to ~150 μm.

3. Results and discussion

3.1. Zirconium alloy structure changes after modification by LEHCPEB and hydrogenation

X-ray diffraction (XRD) showed decrease in the lattice parameters and crystallite sizes of the irradiated samples, as well as increase in microtension (Fig. 1 and Table 1).

Texture (101) is clearly expressed in the initial state and the degree of preferred orientation is equal to 32%. The angular position of the lines for αZr phase in the diffraction pattern remains unchanged after irradiation by LEHCPEB. There is increase of the intensities ratio of the reflections (100), (101), (102) and (110). This indicates change of crystallographic texture on the samples surface. Firstly, the texture

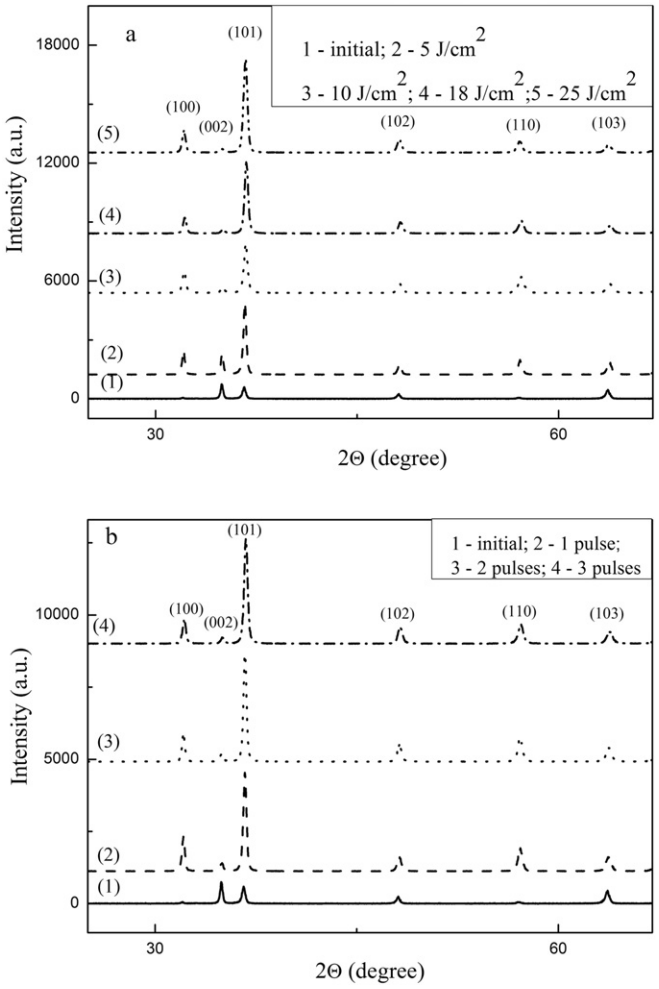

Fig. 1. XRD patterns of the initial samples and samples after LEHCPEB modification at different energy densities (a) and numbers of pulses (b).

may change as a result of solidification since the grains formed during cooling of the melt should grow in the direction of the heat gradient in certain crystallographic directions. Secondly, the thermal stresses arising during rapid cooling cause activation of deformation mechanisms that this in its turn causes changes in the surface texture of the treated by LEHCPEB samples [4]. Broadening of the peak and the presence of thin plates (Transmission electron microscopy data) are the indications of the martensite α′ formation on the treated samples surface. According to XRD data, the structure of the modified samples is a supersaturated solid solution of niobium in the α-modification of zirconium with hcp lattice. The pulses number increases from 1 to 5 results in the significant (more than 3 times) coherent scattering reduction due to structure dispersing. Pulsed impact and subsequent high-speed quenching is a dual recrystallization of phase under conditions very far from equilibrium with large internal stresses raised. The change in the beam energy density also causes increase in the lattice parameters and decrease in the regions of coherent scattering of the samples. It was shown earlier [11] that treatment by 1 pulse leads to the grain size reduction and the grain size increased with the further increase of number of pulses, the grain size also increased with the growth of energy density.

The internal structure of the grains varies greatly as the result of exposure to the LEHCPEB with the above discussed parameters. The structure of the modified alloy unlike the initial material is a martensite (α′-phase). Dimensions of martensite plates range from 0.1 to 0.3 μm (preferably about 0.1 μm). The peculiarity of the formed structure is