Research Article

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Study on microstructure and wear resistance of Zr-17Nb alloy irradiated by high current pulsed electron beam

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Abstract: In this paper, the microstructure and wear resistance of Zr-17Nb alloy treated by high current pulsed electron beam were studied in detail. A phase change occurs after pulse treatments using X-Ray Diffraction (XRD) analysis, showing \( \beta \) (Nb) phase and \( \alpha \) (Zr) phase transformed by a part of \( \beta \) (Zr, Nb) phase. Also, narrowing and shifting of \( \beta \) (Zr, Nb) diffraction peaks were found. Scanning Electron Microscope (SEM) and metallographic analysis results reveal that the microstructure of alloy surface before high current pulsed electron beam (HCPEB) treatment is composed of equiaxed crystals. But, after 15 and 30 pulse treatments, crater structures are significantly reduced. Besides, it was also found that the alloy surface has undergone eutectoid transformation after 30 pulse treatments, and the reaction of \( \beta \) (Zr, Nb) \( \to \) \( aZr + \beta Nb \) had occurred. Microhardness test results show that microhardness value presents a downward trend as the number of pulses increases, which is mainly due to the coarsening of the grains and the formation of a softer \( \beta \) (Nb) phase after phase transformation. The wear resistance test results show that the friction coefficient increases first, then decreases and then increases with the increase of pulse number.

Keywords: Zr-Nb alloy; high current pulsed electron beam (HCPEB); surface modification; eutectoid reaction; wear resistance

1 Introduction

There are many types of phase transitions involved in the processing of Zr-based alloy, and these phase transitions have an important impact on the properties of the material [1]. Ma et al. [2] studied that after a series of processing and recrystallization heat treatment, Zr\(_4\)Sn was precipitated as a new dispersed phase, which greatly improved the mechanical properties of the material. Li et al. [3] annealed Zr-2.5Nb under air cooling conditions. Zirconium alloy was transformed into a strengthening phase of \( \omega \)-phase, and subsequently transformed into a stable \( \alpha \)-phase gradually and \( \beta \) phase in the heat preservation process, which altogether led to increase its strength. Therefore, the mechanical properties can be significantly improved by controlling the phase transitions during Zr-based alloy processing. Besides, Zr element can also refine the crystal grains, and form a solid solution or a second phase with other alloying elements. The presence of these phases can significantly improve the tensile strength and creep resistance of the alloy. Zr-based alloys have high corrosion resistance in high-temperature aqueous solutions, good mechanical properties, and resistance to radiation damage, which are widely used in aerospace [4], military [5], nuclear reaction [6], chemical engineering [8], marine engineering, medicine [8], biology and so on [9]. At present, many research scientists are shifting their focus to the mechanical properties of Zr-based alloys to expand further the application potential of Zr in the structural field [10–13]. However, the mechanical properties of these alloys are poor, including their ultimate tensile strength (less than 900 MPa), which does not meet the requirements of engineering applications. Therefore, there is an urgent need to develop and explore new types of zirconium alloys. Nb is one of the most important alloying elements in advanced Zr-based cladding materials for nuclear power plants [14]. The corrosion resistance can be improved by adding Nb, and the Zr alloy composition can be optimized [15]. According to the binary phase diagram of Zr-Nb alloy (as indicated in Figure 1), solid-phase begins...
to precipitate when the temperature of the melt drops to 1750°C, thereby solid-liquid coexistence zone is crossed as temperature of melt further decreases, and β (Zr, Nb) solid solution is formed at 1720°C. α-Zr phase begins to precipitate when the temperature further decreases to 650°C, and the eutectoid reaction can be expressed in Eqs.1 when the temperature further reduces to 620°C. Finally, α-Zr and β-Nb phases are generated when the temperature is cooled to room temperature

$$\beta\text{(Zr, Nb)} \rightarrow aZr + \beta\text{Nb} \quad (1)$$

High current pulsed electron beam (HCPEB) is an emerging surface modification technology in the decades, which has the advantages of high efficiency, simplicity, reliability, and good repeatability. Under the action of HCPEB, high energy ($10^8$–$10^9$ W/cm$^2$) is deposited in a very thin layer (less than tens of microns) in a short time (a few microseconds), which results in a very fast surface heating and cooling and thermal stress. As a result, a large number of metastable microstructures or phase structures, such as supersaturated solid solutions [17], ultrafine grains [18] and nanostructures [19]. Therefore, it has widely attracted attention from many researchers [20]. Rapid melting and solidification processes on the material surface are caused in the process of HCPEB treatment, resulting in the formation of ultrafine grain structures. These structures possess excellent properties that cannot be obtained with conventional treatment methods. Zou et al. [21] studied the martensite transformation of AISI D2 steel by a high current pulsed electron beam, and found that HCPEB can suppress the martensite transformation on the steel surface and achieve austenitizing and nanocrystallization of the material surface, increasing the surface hardness and corrosion resistance of D2 steel. Hao et al. [22] bombarded WC-6%Co cemented carbide with high current pulsed electron beam and found that WC phase decomposed into ultrafine crystals of WC$_{1-x}$ phase and nanographite with increasing pulse numbers, ultrafine crystal carbides help improve the surface microhardness and wear resistance.

Chai et al. [23] investigated the microstructure of zirconium alloys irradiated by HCPEB and found that the microstructure is refined and the texture is significantly enhanced under the action of HCPEB, leading to the continuous increase in microhardness. Yang et al. [24] treated Zr-702 zirconium alloy with HCPEB and found that a martensite phase transformation, high-density dislocations and deformed twins appear in the remelted layer. As a result, surface microhardness and corrosion resistance have been significantly improved due to the above structures. According to the above study, phase transformation induced by HCPEB has a significant effect on the hardness and corrosion resistance of the alloy. Additionally, few literatures have reported on zirconium-based alloys rich in β-phase stable elements (such as Nb, and Hf elements) by HCPEB treatment [25]. Therefore, this paper investigates phase transitions and surface microstructure generated on Zr-17Nb alloy induced by HCPEB, as well as the effect of microstructure on wear resistance and hardness of alloy surface is also inspected under the action of HCPEB.

## 2 Experimental

### 2.1 Preparation of Zr-based alloys

The following raw materials were selected for this experiment: high-purity zirconium (Zr ≥ 99.99 wt.%) and high-purity niobium ingot (Nb 99.99 wt.%). Before smelting, the raw materials were cut into small ingots using a sawing machine, and then the small ingots were polished and cleaned by 400# sandpaper and ethanol, respectively. Finally, they were stored in a vacuum drying oven to prepare them for smelting.

Under the protective atmosphere of argon gas, drying raw materials were put into the cold crucible of the induction suspension melting furnace for suspension melting.

The obtained ingot was homogenized in an argon atmosphere at 1373 K for 6 h and then quenched with water. The obtained ingot was subjected to solution treatment (ST) under a vacuum of 1123 K for 1 hour, and then quickly quenched in ice water.

The obtained ingots were cut into a cylinder of $\Phi 10$ mm × 5 mm after the solution treatment. The obtained sam-

**Figure 1: Binary phase diagram of Zr-Nb alloy (at.%) [16]**
2.2 HCPEB treatment

For surface modification of materials, the high current pulsed electron beam device; HCPEB type MMLAB-HOPE-I (made by Dalian university of technology in China) was used. The processing parameters under which this was done are as follows: the vacuum degree of vacuum chamber $6 \times 10^{-3}$ Pa, the acceleration voltage 30 kV, the energy density $4 \, \text{J/cm}^2$, the pulse frequency 0.2 Hz, the pulse duration 3 µs, the target distance 13.5 cm, and the pulse numbers of 5, 15, and 30, respectively.

2.3 Microstructure characterization and performance analysis

In the experiment, the morphology of alloy surfaces before and after HCPEB treatment was observed using an S-4800 field emission scanning electron microscope (made by Hitachi in Japan) and an inverted metallographic microscope of type GX71 (made by OLYMPUS in Japan). The phase composition of the Zr-17Nb alloy surface before and after HCPEB treatment was analyzed using an Ultima IV multi-purpose X-ray diffraction (XRD) system (made by Japanese Science in Japan).

The XRD diffraction system adopted Cu target and Ka radiation, corresponding to X-ray characteristic wavelength of $\lambda = 1.5406$ Å and graphite monochromator filtering, the scanning step length was $0.02^\circ$, the accelerating voltage was 40 kV, the current was 100 mA, the scanning range was $10 - 90^\circ$, and the scanning speed was $7^\circ$/min. The microhardness of alloy surface was measured by FMARS9000 Vickers hardness tester (made by FUTURE-TECH in Japan) before and after the HCPEB treatment. The experimental conditions for microhardness measurement were a loading weight of 100 g and a holding time of 10 s, respectively. When measuring microhardness, take 3 samples for each corresponding pulse number, place a dot on each sample, and finally take the average value. Finally, the friction test was carried out to measure the friction coefficient of the sample surface before and after HCPEB modification using a multifunctional material surface performance tester of type MFT-4000 (made by Huahui Instrument Technology Company in China). The experimental parameters were a loading weight of 10 g, with a reciprocating length of 5 mm, and a reciprocating time of 20 min, respectively. The friction pair of $\text{Si}_3\text{N}_4$ ball with a diameter of 6 mm was adopted. Three samples are taken for each pulse number of friction coefficient, and one average value is taken for each sample.

3 Results and discussions

3.1 Phase analysis of XRD

X-ray Diffraction (XRD) patterns of Zr-17Nb alloy surface before and after HCPEB treatment are shown in Figure 2. It can be concluded from Figure 1 that the phase composition of alloy sample without HCPEB treatment consists of a single phase for $\beta$ (Zr, Nb) solid solution. There is no obvious phase change in the surface layer of the material with 5 pulse treatment. While after 15 and 30 pulse treatments, $\alpha$ Zr and $\beta$ Nb phases are generated, indicating the decomposition of $\beta$ (Zr, Nb) solid solution, as shown in Figure 2(a).

The above results demonstrate the phase transition generated after HCPEB treatment. Further verify that the eutectoid transformation can occur during the rapid cooling and solidification process [26]. Zr and Nb atoms are desolventized from the crystal lattice of $\beta$ (Zr, Nb) phase and the eutectoid transformation of $\beta$ (Zr, Nb) phase occurs, resulting in the formation of $\alpha$-Zr and $\beta$-Nb phases. This eutectoid transformation requires the diffusion of atoms and the interaction between the two phase interfaces generated to form a eutectoid microstructure. Moreover, it is also found from the XRD pattern that only a part of $\beta$ (Zr, Nb) phase is transformed into $\alpha$-Zr and $\beta$-Nb phases. That is because, for a complete transformation into $\alpha$-Zr and $\beta$-Nb phases, it would take a long time of eutectoid transformation. The eutectoid transformation originates from the grain boundary and develops rapidly with the increase of heating temperature [27]. The extremely fast cooling rate induced by HCPEB makes it difficult to continue to provide enough energy required for eutectoid transformation. As a result, $\alpha$-Zr, $\beta$-Nb and $\beta$ (Zr, Nb) phases are formed after the HCPEB treatment.

Compared with the original sample, the diffraction peak of $\beta$ (Zr, Nb) phase shifts and narrows, as shown in Figure 2(b). The diffraction peak of this phase shifts slightly to a high angle as pulsed number increases. This phenomenon is attributed to residual compressive stress in the remelted layer, resulting in decreasing of lattice constant for $\beta$ (Zr, Nb) phase, as shown in Figure 3 [28, 29].
Moreover, the narrowing diffraction peak for $\beta$ (Zr, Nb) phase indicates the coarsening of grain, causing a decrease in hardness, that is, a softening phenomenon occurs, which will have a good effect on the plastic forming and enhance the plasticity of Zr-based alloy. Yan et al. [30] treated 2024Al alloy by high-current pulsed electron beams and found that the phenomenon of coarse grains on the alloy surface and cross-sectional structure is due to the secondary recrystallization process of the alloy surface structure, The main reason is that abnormal grains grow at a higher speed and at the expense of neighboring grains, epitaxial growth occurs during the rapid solidification process, thereby leading to grain coarsening [31, 32].

3.2 Microstructure analysis of Zr-17Nb alloy before HCPEB modification

The metallographic image of Zr-17Nb alloy after solution treatment is shown in Figure 4. It can be seen from Figure 4 that the Zr-17Nb alloy in the original microstructure is mainly composed of equiaxed grains, and their average grain size is 47 $\mu$m using Image J software.

The alloy sample after solution treatment has a smooth surface with clearly visible grain boundaries, no apparent defects, no impurities and no second phase particles. Combined with XRD analysis, it can be determined that the equiaxed crystal is the $\beta$ (Zr, Nb) solid solution phase.

![Figure 2: XRD patterns of Zr-17Nb alloy surface before and after HCPEB treatment Complete XRD pattern; (b) Enlargement of XRD pattern in Figure 2(a)](image)

![Figure 3: Change of lattice constant for $\beta$ (Zr, Nb) phase without and with HCPEB treatment](image)

![Figure 4: Metallographic image of Zr-17Nb (ST) sample without HCPEB treatment](image)
3.3 Microstructure analysis of Zr-17Nb alloy after HCPEB modification

The surface morphology of Zr-17Nb alloy after HCPEB treatment are shown in Figure 5. It can be seen in Figure 5(a) that crater structures appear after 5 pulses, which are common structures obtained by HCPEB. The formation mechanism of crater structures is explained as follows: when the HCPEB bombards the material surface, the subsurface layer of the material melts first, and then the molten liquid generated will result in rapid volume expansion. Finally, a volcanic crater morphology is formed [33, 34]. In addition, it is found from the enlargement of Figure 5(a) that the Nb element is dissolved in Zr matrix to form a β (Zr, Nb) solid solution [35] after HCPEB treatment. Compared with the original microstructure (the average size of grain for β (Zr, Nb) solid solution is 47 µm), the grain size of this phase is approximately 60 µm, indicating that grain coarsening occurs after HCPEB modification, as shown in Figure 5(b). Compared with alloy sample of 5 pulses, the volcanic craters remelt after 15 pulse treatments, as shown in Figure 5(c). The increasing energy provides a sufficient duration for the molten state, causing the previously generated crater to be refilled with flowing liquid.

Figure 5: SEM images of Zr-17Nb (ST) sample without HCPEB treatment (a) crater structures, 5 pulses, low magnification; (b) partial enlarged image of Figure 5(a), 5 pulses, high magnification; (c) partial remelting of crater structures, 15 pulses, low magnification; (d) Surface defects, 15 pulses, high magnification; (e) surface microstructure, 30 pulses, low magnification; (f) surface defects, 30 pulses, high magnification
Therefore, the density of craters and surface roughness of alloy decreases [36, 37]. At the same time, material surface remelted after 15 pulse treatments, and equiaxed crystals of $\beta$ (Zr, Nb) phase are regrown on the surface due to rapid cooling effect. Moreover, some defects can be seen on the surface, as shown in Figure 5(d). The surface morphology becomes lumpy after 30 pulses, as shown in Figure 5(e), and the grain size of equiaxed crystals for $\beta$ (Zr, Nb) solid solution is calculated to be 50 $\mu$m (using a software), which is not much different from the grain size of equiaxed crystals of 47 $\mu$m for the original sample. From the above results, it is observed that surface microstructure after HCPEB modification does not exhibit obvious refinement. Some defects occur after 30 pulses, as shown in Figure 5(f), which is the result of alloy sample after 15 pulses.

The surface morphology of the eutectoid microstructure generated after 30 pulses is shown in Figure 6. It is found that the eutectoid microstructure presents a lamellar structure, similar to lamellar pearlite. The lamellar spacing is calculated to be 1.5 $\mu$m using statistical software.

This microstructure is verified by XRD analysis in section 3.1. The solid solution of $\beta$ (Zr, Nb) phase undergoes eutectoid transformation, causing $\beta$ (Zr, Nb) phase decomposed into $\alpha$-Zr and $\beta$-Nb phases after 30 pulses. The eutectoid transformation in this paper is different from eutectoid transformation under conventional cooling conditions. In our experiment, this transformation called the active eutectoid transformation occurs under the condition of rapid cooling induced by HCPEB. Active eutectoid occurs in near-eutectoid zirconium and titanium alloys, and its decomposition rate is extremely fast, and even rapid quenching cannot suppress this phase transformation [38]. Donthula et al. [39] studied the active eutectoid transformation of hypereutectoid Ti-12at.\% Cu alloy. Under the ultra-high cooling conditions, $\alpha$ Ti and wattle Ti$_2$Cu phases nearing equilibrium composition are formed through active eutectoid transformation. Rapid quenching may promote this active eutectoid transformation. Moreover, this transformation contributes to the improvement of antibacterial property in biomedicine. Brice et al. [40] found that $\beta$-Ti decomposes into $\alpha$-Ti phase and Ti$_2$Zn phase through active eutectoid transformation in water-quenched Zn-47 wt.% Ti alloy. The aggregation state of the decomposition products is flaky, and a good pearlite structure can be obtained under rapid cooling conditions. At the same time, the active eutectoid reaction is not a stable phase.

### 3.4 Microhardness analysis

The change of microhardness for Zr-17Nb alloy surface before and after HCPEB modification is shown in Figure 7. As can be seen from Figure 7, the microhardness values of the Zr-17Nb alloy surface decreases significantly with the increase of pulsed number, from 233.4HV of original sample

![Figure 7: The change of microhardness for Zr-17Nb alloy surface before and after HCPEB modification](image)
to 188.0HV of alloy sample with 30 pulse treatments. The phenomenon for decreasing microhardness is mainly attributed to the coarsening of grain, which is corresponding to the result of XRD analysis [41]. Moreover, a soft phase of $\beta$-Nb is produced due phase transition induced by HCPEB, contributing to decreasing microhardness.

### 3.5 Wear resistance analysis

The change of friction coefficient for Zr-17Nb alloy surface before and after HCPEB modification is shown in Figure 8. It can be seen from Figure 8 that the friction coefficient of alloy surface first increases, then declines and then increases with increasing pulse number.

![Figure 8: The change of friction coefficient for Zr-17Nb alloy surface before and after HCPEB modification](image)

The friction coefficient of the alloy surface is highest at 5 pulses, indicating worst wear resistance. While this value is lowest at 15 pulses, demonstrating the best wear resistance. The wear resistance of alloy surface also deteriorates after 30 pulses. The worst wear resistance of the 5-pulsed sample is attributed to a large number of crater structures and a decrease of microhardness on the material surface. Crater structures will make the surface rough, resulting in dramatic abrasion in initial stage of abrasion for alloy surface. Therefore, the friction coefficient of the 5-pulsed sample increases. The crater density is significantly decreased after 15 pulses, reducing extent of abrasion in initial stage of abrasion. As a result, the electron beam can significantly improve the wear resistance of the alloy surface [42, 43]. Xue et al. have found that by improving the friction and wear properties of Zr alloy, potential applications of Zr alloy in special fasteners for petroleum engineering can be explored [44, 45]. Xu et al. have made Zr alloy a strong candidate for orthopedic implant materials by improving its wear resistance [46]. The microhardness of alloy surface after 30 pulses is lower than that of other alloy samples, and a softer phase of $\beta$-Nb is produced by HCPEB, thus resulting in weaker ability to resist external forces. Therefore, the wear resistance of alloy surface will deteriorate.

![Figure 9: The abrasion loss of alloys for Zr-17Nb alloy surface before and after HCPEB modification](image)

The abrasion loss of alloys for Zr-17Nb alloy surface before and after HCPEB modification is shown in Figure 9. We can see from the data of abrasion loss that as the number of pulses increases, the value of abrasion loss first increases and then decreases, and finally increases again at 30 pulses. The above result shows that the wear resistance is the best at 15 pulses [47, 48].

### 4 Conclusions

In summary, the microstructure and properties of Zr-17Nb alloy are changed significantly by HCPEB treatment. The experimental results in this paper are as follows:

1. XRD analysis indicates that a phase change occurs after 15 and 30 pulse treatments, showing the $\beta$-Nb phase and $\alpha$-Zr phase transformed by a part of the $\beta$ (Zr, Nb) phase. Also, narrowing and shifting of $\beta$ (Zr, Nb) diffraction peaks are found.
2. SEM and metallographic analysis results reveal microstructures of alloy surfaces without HCPEB treatment are composed of equiaxed crystals. Moreover, the grains grow after 5 pulse treatments. After 15 and 30 pulse treatments, crater structures have significantly been reduced, demonstrating decreasing surface roughness as pulse numbers increase. Besides, it has also been found that alloy surface has undergone eutectoid transformation after 30 pulse treat-
ments, and the reaction of $\beta$ (Zr, Nb) $\rightarrow$ $\alpha$ Zr + $\beta$ Nb has occurred.

3. Microhardness test results show that microhardness value presents a downward trend as the number of pulses increases, which is mainly due to the coarsening of the grains and the formation of a softer $\beta$ (Nb) phase after phase transformation.

4. The wear resistance test results show that the friction coefficient increases first, then decreases and then increases with increasing pulse number, indicating the best wear resistance of alloy surface with a friction coefficient of 1.384 at 15 pulse treatments.

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References


