Journal of Materials Science and Chemical Engineering, 2016, 4, 46-57
http://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

Research on the Surface Modification of Pure Zirconium by Electron Beam

Jinxin Ma, Kemin Zhang*, Xiaolin Zhang, Yu Wang

College of Materials Engineering, Shanghai University of Engineering Science, Shanghai, China
Email: *zhangkm@sues.edu.cn

How to cite this paper: Ma, J.X., Zhang, K.M., Zhang, X.L. and Wang, Y. (2016) Research on the Surface Modification of Pure Zirconium by Electron Beam. *Journal of Materials Science and Chemical Engineering*, **4**, 46-57.
http://dx.doi.org/10.4236/msce.2016.412006

Received: November 3, 2016
Accepted: December 5, 2016
Published: December 8, 2016

Abstract

In this paper, the changes of surface morphology, microstructure, hardness and corrosion resistance of industrial pure zirconium before and after surface modification by high current pulsed electron beam were discussed. The microstructure evolution and surface morphologies of the samples were characterized by using X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM). The experimental results show that sample by high current pulsed electron beam treatment surface melting, martensitic phase transformation occurred, and volcanic crater morphology and fine microstructure in the remelted layer surface; with the increase of number of pulses, after processing the microhardness of the samples also with the increase, 15-pulsed sample microhardness than the original sample increased by 30.9%. Corrosion resistance of samples was studied with the impedance diagram and polarization curve. The electrochemical results show that corrosion resistance of samples by high current pulsed electron beam treatment presents different degrees of change, the 5-pulsed sample in 1 mol HNO_3 solution corrosion of the best, and 15-pulsed sample corrosion resistance is even lower than the original sample. Grain refinement, martensite transformation, dislocation and deformation twins are the main reasons for improving the micro hardness and corrosion resistance of the samples.

Keywords

Pure Zirconium, Pulsed Electron Beam, Surface Modification

1. Introduction

Commercially pure zirconium is composed of 99.2% - 99.9% zirconium + hafnium. It has been widely used in severely corrosive environments as structural material because of its excellent corrosion resistance. Zirconium is an excellent structural material for

nuclear reactor, nuclear fuel package materials, strong corrosion resistant materials, biomedical materials and new functional materials [1] [2] [3]. At present, most of zirconium materials used in water cooled nuclear reactors, the second major application areas for the chemical processing industry.

High current pulse electron beam (HCPEB) is a new type of highly efficient material surface treatment method, which has the advantages of high energy utilization rate, controllable process, no pollution, etc.. In the strong flow pulse electron beam irradiation process, the surface of the substrate can reach very high energy density (10^8 - 10^9 W/cm^2) in a very short period of time, resulting in a high temperature melting of the surface heating and evaporation, followed by rapid cooling [4] [5]. Through this condensation process, the metal surface will produce a dynamic stress region to make its surface modification, in this process, the material surface will appear hundreds of microns deep crater. After irradiation, a large number of fine grains and nano structure can be obtained, and the phase transition and structural changes can also occur. Finally, the mechanical properties and corrosion resistance can be improved effectively.

Due to the condition of metal zirconium in the application process is more severe, it is necessary to put forward more strict requirements on the safety, reliability and economy of structural materials. Therefore, further improve the mechanical properties of zirconium metal and corrosion resistance and prolong the service life, reduce maintenance costs, has become an important issue, and electron beam surface modification technology plays an important role in promoting. The purpose of this experiment is to study the influence of pulse electron beam treatment on the surface morphology, microstructure, micro hardness and corrosion resistance of zirconium [6] [7].

2. Experimental Procedures

This experiment uses the Zr-1 type industrial pure zirconium. The chemical composition of the material sees **Table 1**.

The electric spark wire cutting diameter with 15 mm thickness is 2 mm sample, sand will be polished specimen surface, polished to a mirror and the sample is placed in the acetone solution cleaning, which is then placed in the MMLAB-HOPE-I high current pulsed electron beam device for irradiation treatment, experimental parameters: electron beam energy of 20 keV, 4 J/cm^2 energy density, pulse time interval for 30 seconds, target distance is 140 mm, vacuum 6.0×10^{-3} Pa, pulse number respectively 5 times, 15 times.

The sample surface morphology after pulse treatment was observed by the super depth of field microscopy of VHX-600 and scanning electron microscope (SEM) of AS-3400; with Shimadzu D-6000 type X-ray diffraction analysis processing after the specimen surface phase structure (Cu target, scanning range 20 - 90 degrees); the

Table 1. Composition analysis of pure zirconium (mass fraction, %).

Element	Zr + Hf	Hf	Fe + Cr	H	N	C	O
Content	≥99.2	≤4.5	≤0.2	≤0.006	≤0.025	≤0.05	≤0.10

HX-1000 microhardness tester were measured before and after treatment in the two samples of hardness value, select the load of 10 g, 25 g, 50 g, 100 g, loading time for 15 seconds. The specimen before and after electron beam treatment dynamic potentiodynamic anodic polarization curves was measured by the CHI660E electrochemical system, reference electrode and saturated calomel electrode, auxiliary electrode of Pt, the working electrode as samples, scan rate 0.005 V/s, test using the test level 1 mol HNO_3 solution. The solution is naturally placed in the air and the temperature is controlled at 37˚C ± 0.5˚C. Test the sample into the test solution for about 20 minutes, then the polarization curve test is carried out after the open circuit voltage is stable.

3. Experimental Results and Analysis

3.1. XRD Analysis

As is shown in the Figure 1, the structure of pure zirconium phase is changed obviously before and after electron beam treatment. According to the $2d\sin\theta = \lambda$, 15 pulses sample and 5 pulses sample was increased than raw material point of view, can get d becomes smaller, which can derive that grain size increases, the grains can be refined. To compare 5 pulses sample and 15 pulses sample of diffraction peak width at half height, 15 pulses of half high width become larger, according to Scherrer formula $D = K\lambda/B\cos\theta$, indicating that the 15 pulses sample grain more refinement. Due to the component for pure zirconium, diffraction peaks are just corresponding a hexagonal phase, but the combination of electron beam treatment after the surface morphology and found that appeared in the alpha phase, which is due to electron beam rapid heating and cooling solid solution transformation of the cubic crystal, electron beam processing makes the material surface layer temperature above 850˚C, will change the body centered cubic beta phase, and with the rapid increase in temperature, martensitic

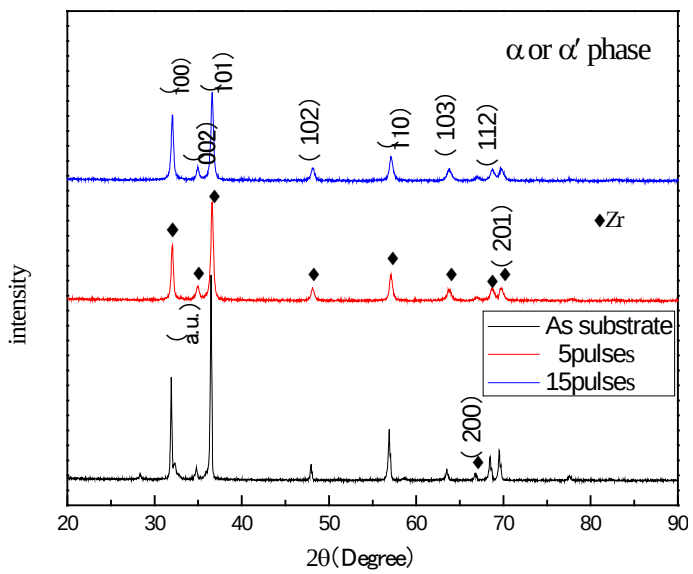

Figure 1. X-ray diffraction analysis of pure zirconium under different pulse times.

transformation, transformation to alpha phase. At the same time, after the electron beam treatment, (101) (110) (100) the intensity of the crystal surface is decreased, and the intensity of the diffraction peak becomes lower. The possible reasons are as follows: 1) The electron beam treatment is generally resolidified along the direction of the thermal gradient; 2) Martensitic transformation can also cause the change of the six square phase distribution; 3) At the same time, the diffraction peak becomes wider, and the angle of the diffraction peak shifts to the right, which indicates that the electron beam pulse processing makes the grain refinement [8] [9] [10].

3.2. OM Morphology Analysis

Figure 2 shows the optical morphologies of Zr-1 samples after HCPEB irradiation with different pulses. From the figure can be clearly observed typical crater morphology. After electron beam bombardment, the surface of the specimen first began to melt and internal melting, the volume of rapidly expanding, thus leading to surface similar to the eruption of the volcano. Eventually lead to producing crater shaped crater. And material surface apparent wave morphology, which is due to the electron beam treatment surface melting and solidification, Comparison of 1 and 2 can also find that the surface of the sample is more smooth after the 15 pulse treatment, with the increase of number of pulses, inevitable meeting so that the electron beam bombardment is more uniform, inject more energy, the surface liquefaction is more uniform, eventually leading to the increase of surface roughness [11].

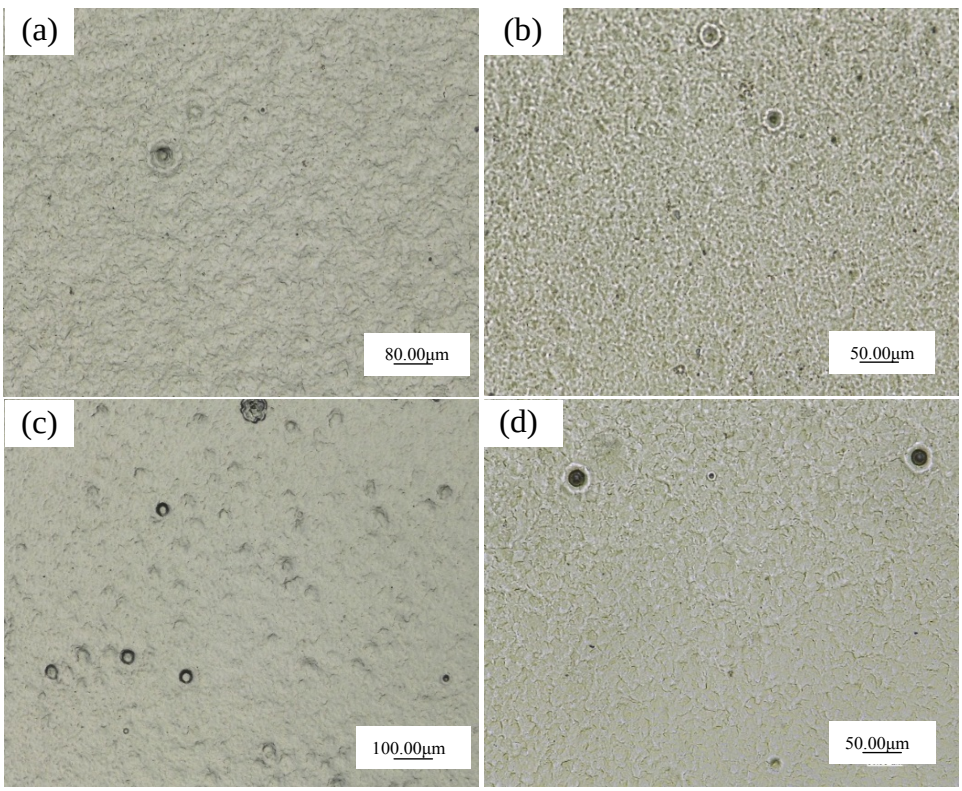

Figure 2. Optical morphologies of Zr-1 samples after HCPEB irradiation with different pulses.

3.3. SEM Morphology Analysis

Respectively, compared **Figure 3(a, c)** and **Figure 3(b, d)** two figures, a certain fold morphologies appears on the 5-pulsed sample surface, and the direction is not fixed. In the figure did not see the emergence of volcanic craters, however, through the optical microscopy photos can be seen a certain number of volcanic craters. The wrinkles on the surface of the sample after the 15 pulse treatment were flat compared with the samples treated with 5 pulses. The appearance of the fold is due to the direction of the electron beam and the heat flux in the same direction, and the final solidification morphology is also similar to a directional solidification [12] [13].

According to the scanning electron microscope (SEM) can be seen in figure, with the increase of number of pulses, the folds of the sample surface will tends to decrease. This is because with the increase in the number of pulses, the impact of the electron beam on the sample surface more uniform, the energy distribution is more uniform, so that the surface smooth.

The cross section morphology of the sample before and after electron beam treatment is shown in **Figure 4** Compared with the original specimen, after treatment of the specimen cross-section under the scanning electron microscope showed three different regions: white remelting layer, solid phase transition layer of a lamellar martensite, heat affected zone. The solid phase transition layer is a part of the heat affected zone. It is worth noting that the thickness of the middle layer increases with the increase of the number of pulses. In the process of electron beam treatment, the heat in the surface

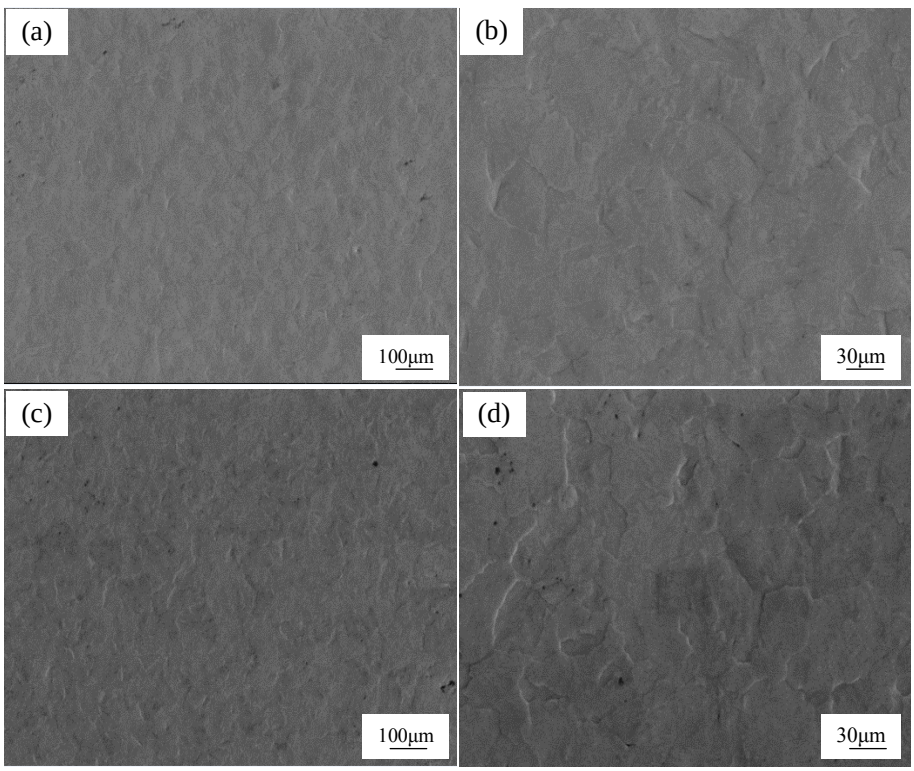

Figure 3. SEM morphology of different pulse treatment.

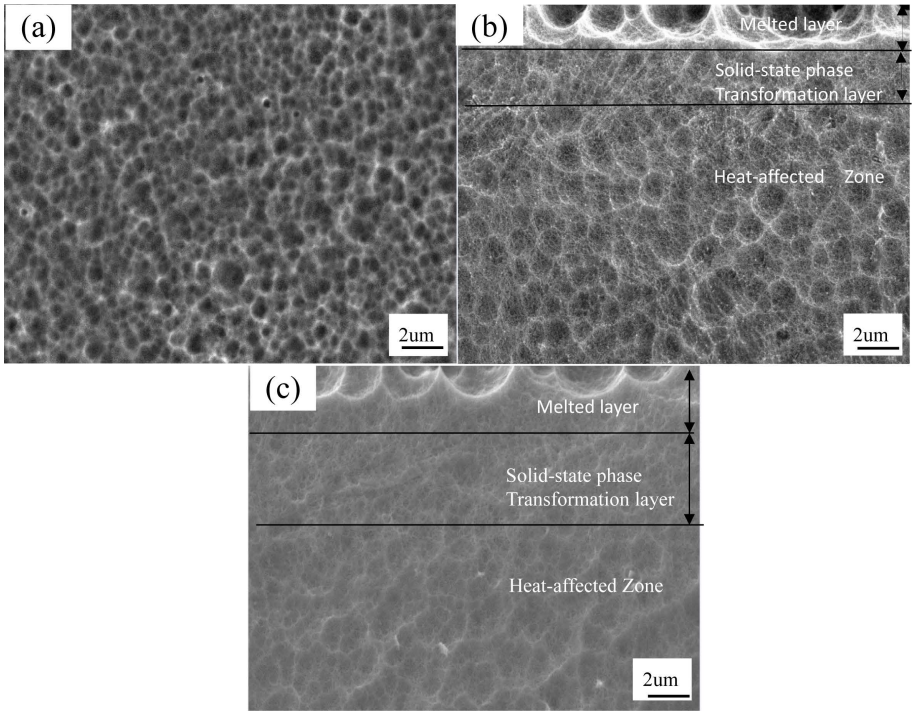

Figure 4. The cross section SEM morphology of the sample before and after electron beam treatment.

layer will be diffused in the surface [14]. If the temperature is lower than the remelting layer, it is not enough to reach the melting point, which will greatly inhibit the process of martensite transformation in the process of electron beam treatment. At the same time, with the increase of the number of pulses, the subsurface of the sample to accumulate a large amount of heat, and the deeper place. In this case, with the increase of the number of pulses, the depth of the solid phase transition layer of martensite will increase.

3.4. Hardness Analysis

Figure 5 shows a different number pulses surface processing under different load hardness comparison chart. By comparison, we can see, after pulsed electron beam treatment, hardness under different load is compared, compared with that before the treatment has increased. From the bar chart can be seen loading is 50 g, 15 pulses sample surface hardness is improved greatly, compared to the substrate increased by 30.9%, and 5 pulses sample only than that of the substrate increased 16.5%; while the load is 100 g, 150 g, 200 g, 5 pulses sample and 15 pulses sample are compared to the substrate improved a lot and the improvement of roughly the same degree.

Figure 6 for the sample under the load of 50 g different pulse number of section hardness distribution figure and the cross-sectional microhardness is complex fluctuations in the trend, under the surface of hundreds of microns range appeared increased the microhardness, 15 times pulse increased the hardness of the sample than 5 times pulse of the specimen, when the depth reaches a certain degree of hardness distribution

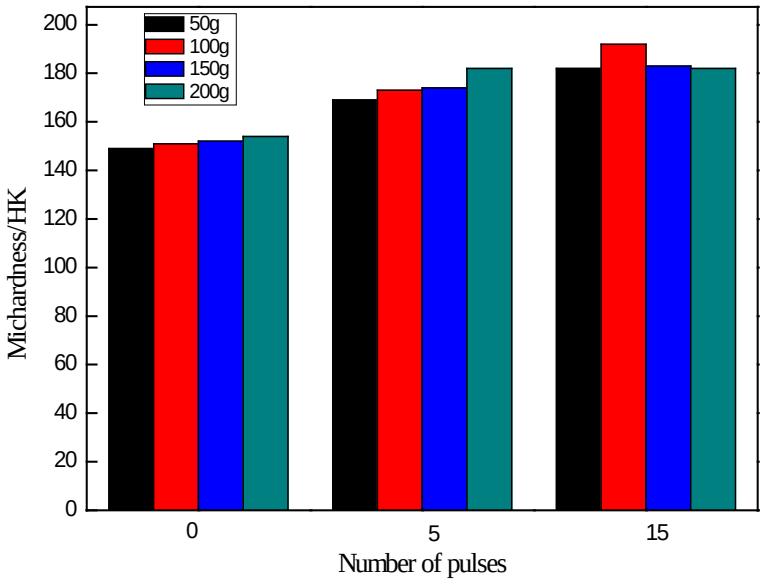

Figure 5. Surface hardness of Zr-1 samples before and after HCPEB irradiation.

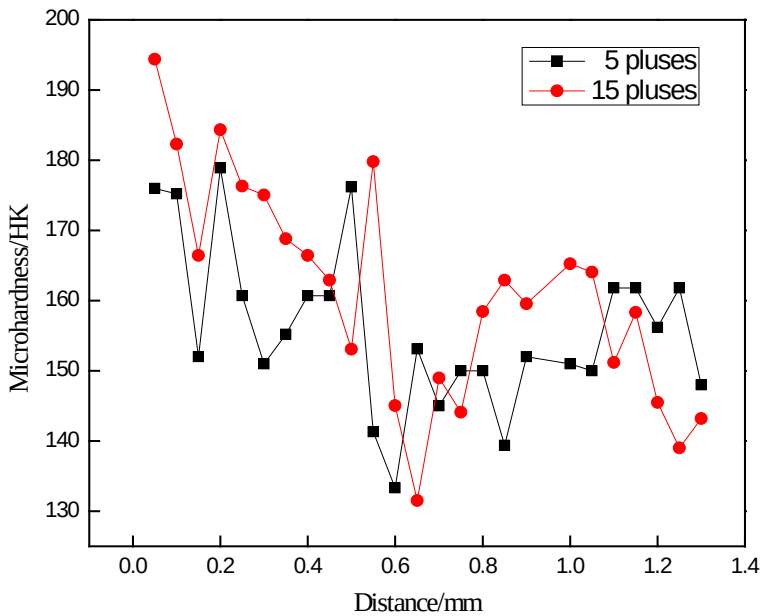

Figure 6. Cross section hardness distribution of pure zirconium under the same load.

of large fluctuations, which is specimens due to the electron beam processing, surface melting in the process of thermal shock wave formation and spread to a deeper region and heat affected zone, resulting in material surface deformation and work hardening effect. So in comparison, under the 50 g load, the hardness of the sample after the 15 pulse processing is greater, the effect is better. Remelting layer of grain refinement and martensitic phase transformation strengthening and deformation twins can improve the surface micro hardness materials; on the other hand, with the increase of number of

pulses, a large number of deformation twins resulting, these are main factors to improve the microhardness.

3.5. Corrosion Resistance Analysis

Figure 7 shows the EIS of Zr-1 samples in 1 mol HNO_3 before and after HCPEB irradiation. Figure 7(a) displays the relationship between impedance magnitude |Z| and frequency f, and the impedance magnitude of different frequency can be read out directly. It can be clearly seen from the figure that the impedance value at different frequencies. The high-frequency region of the figure shows the electrolyte impedance between the sample and the reference electrode. The impedance of the region is independent of the frequency, and the low frequency region is the polarization resistance of the sample. But at the low frequency limit, the impedance is attributed to the polarization resistance

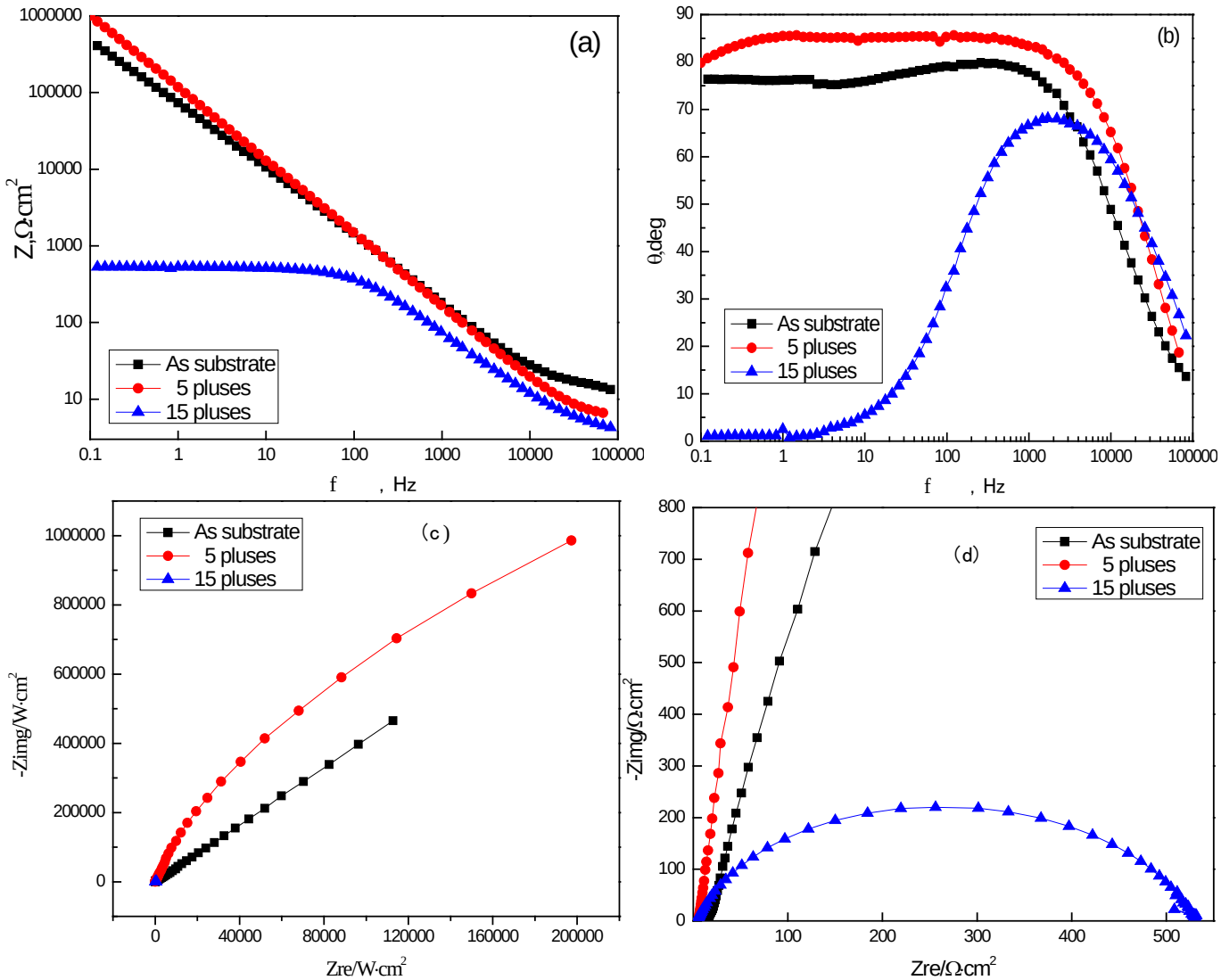

Figure 7. EIS of Zr-1 samples in 1 mol HNO_3 before and after HCPEB irradiation: (a) Impedance and frequency, (b) Phase angle and frequency, (c) Nyquist plot, (d) Local magnification of (c).

of the sample in the electrolyte [15]. The corresponding curves in low frequency region (10^{-1} Hz) show clearly that the polarization impedance values of the samples after electron beam treatment showed different degrees of change. Especially for the 5-pulsed sample, the polarization impedance value at the place of 0.1 Hz has increased by nearly 1000 times to the 15-pulsed sample, and larger than the original sample impedance value. **Figure 7(b)** shows the relationship between phase angle theta and frequency f, from the figure can be seen in the low frequency region 5 times pulse phase angle of the sample maximum is close to 90 degrees, showing obvious a near capacitive behavior, at this time, the surface of the pulsed sample is in a passive state in HNO_3 solution, and 15 times pulse sample in the low frequency region of minimum phase angle close to 0 degrees, indicating that this specimen of the oxide film may be subject to corrosion and corrosion efficiency greatly reduced. However, the near capacitive behavior hardly appeared in the initial sample, suggesting that the oxide film on the irradiated sample surfaces can maintain its characteristic response over a longer period of time [16] **Figure 7(c)** is Nyquist plot (**Figure 7(d)** is the low frequency area of the amplification figure), from the **Figure 7(c)** can be seen the capacitance arc diameter of 5-plused sample is the largest among all the tested samples, and the capacitance arc diameter of 15-plused sample is the smallest. In general, the greater the diameter of the capacitor arc, the ability of the material to suppress the electron loss of electrons is stronger, the stronger the corrosion resistance. In summary, it can be inferred that after the high current pulse electron beam treatment of the sample, the corrosion resistance of 5-pulsed samples are best, and the 15-pulsed sample's corrosion resistance is lower than the initial sample.

Figure 8 shows different pulse number of samples of the polarization curve, analyzing the curves using the Tafel extrapolation method, can be calculated from the corrosion potential (Ecorr) and corrosion current density icorr, show in **Table 2**. The free

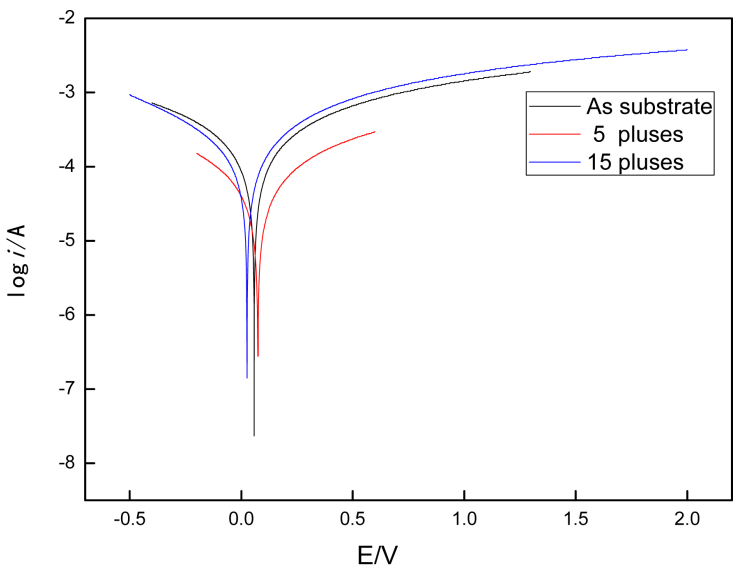

Figure 8. Potentiodynamic polarization curves of Zr-702 samples in 1 mol HNO_3 before and after HCPEB irradiation.

Table 2. Corrosion data of pure zirconium under different pulse times.

Samples	Pulses	E_{corr}(mV)	i_{corr}(μA/cm^2)
As substrate		56.2	289.68
5 pulses	5	73.5	113.71
15 pulses	15	18.3	263.04

corrosion potential of initial samples is 56.2 mV, after 5 pulse treatment increased to 73.5 mV, 15 pulse treatment reduced to 18.3 mV. And the corrosion current density after electron beam treatment also becomes smaller, the 5-pulsed sample corrosion current density decreases by about 2/3 than the initial sample, and the 15-pulsed sample corrosion current density is reduced by about 1/10 than the initial sample. So the corrosion resistance of 5-pulsed sample is better than that 15-pulsed sample. The reason for the improvement of corrosion resistance is mainly due to grain refinement, and the surface clearness is improved after pulse electron beam treatment, which is also beneficial to the improvement of corrosion resistance [17] [18] [19] [20].

4. Conclusions

In this paper, the phase composition, surface morphology and properties of pure zirconium were studied by pulse electron beam treatment, and the changes of surface morphology and properties were obtained:

1) After pulsed electron beam treatment, zirconium metal surface showing folds wave morphology, and with the increase number of pulses, sample surface morphology tended to be smooth. XRD results showed that after the electron beam treatment, the diffraction peak width becomes wider, and the angle of the whole shift to the right, it shows that the grain is refined, and the crystal plane spacing becomes smaller.

2) With the increase of pulses, surface hardness increased gradually. Fine grain strengthening, martensitic phase trans-formation strengthening and deformation twins play a significant role in increasing the surface hardness.

3) Hardness test results show that the surface hardness of samples after two different numbers pulses processing has improved significantly, of which 5 times pulse processing is 1.2 times of that of the matrix, and 15 times pulse processing is 2.6 times of that of the matrix. And under the same load different number pulses, the cross section of the test specimen hardness distribution fluctuations larger, within the range of hundreds of microns are increased the microhardness, of which 15 pulses, the hardness can be significantly improved. This is mainly played the role of strong electron beam treatment after grain refinement.

4) Electrochemical testing results indicate that the impedance value and phase angle of 5-pulsed sample is biggest, indicating that the near capacitive behavior of 5-pulsed sample are best; and the corrosion potential of 5-pulsed sample larger than the initial sample, and the corrosion current density dropped to about 1/3 of the initial sample. Therefore, 5-pulsedsample owned the best corrosion resistance.

References

[1] Sarrail, B., Schrupp, C., Babakhanyan, S., Muscare, K., Foyos, J., Ogren, J., Sparkowich, S., Sutherlin, R., Hilty, J., Clark Jr., R. and Es-Said, O.S. (2007) Annealing and Anomalous (Bimodal) Grain Growth of Zr 702. *Engineering Failure Analysis*, **14**, 652-655. https://doi.org/10.1016/j.engfailanal.2006.02.017

[2] Yau, T.L. (2010) 3.14—Corrosion of Zirconium and its Alloys. *Shreir's Corrosion*, **3**, 2094-2134. https://doi.org/10.1016/B978-044452787-5.00101-3

[3] Abdelkader, A.M., Daher, A., Abdelkareem, R.A. and El-Kashif, E. (2007) Preparation of Zirconium Metal by the Electrochemical Reduction of Zirconium Oxide. *Metallurgical and Materials Transactions B*, **38**, 35-44. https://doi.org/10.1007/s11663-006-9016-z

[4] Proskurovsky, D.I., Rotshtein, V.P., Ozur, G.E., Markov, A.B., Nazarov, D.S., Shulov, V.A., Ivanov, Yu.F. and Buchheit, R.G. (1998) Pulsed Electron-Beam Technology for Surface Modification of Metallic Materials. *Journal of Vacuum Science & Technology A*, **16**, 2480-2488. https://doi.org/10.1116/1.581369

[5] Proskurovsky, D.I., Rotshtein, V.P., Ozur, G.E., Ivanov, Yu.F. and Markov, A.B. (2000) Physical Foundations for Surface Treatment of Materials with Low Energy, High Current Electron Beams. *Surface and Coatings Technology*, **125**, 49-56. https://doi.org/10.1016/S0257-8972(99)00604-0

[6] Hao, S.Z., Gao, B., Wu, A.M., Zou, J.X., Qin, Y., Dong, C., An, J. and Guan, Q.F. (2005) Surface Modification of Steels and Magnesium Alloy by High Current Pulsed Electron Beam. *Nuclear Instruments & Methods in Physics Research*, **240**, 646-652.

[7] Dong, C., Wu, A.M., Hao, S.Z., Zou, J.X., Liu, Z.M., Zhong, P., Zhang, A.M., Xu, T., Chen, J.M., Xu, J., Liu, Q. and Zhou, Z.R. (2003) Surface Nanostructure and Amorphous State of a Low Carbon Steel Induced by High-Current Pulsed Electron Beam. *Surface & Coatings Technology*, **196**, 145-149.

[8] Zou, J.X., Zhang, K.M., Grosdidier, T., Dong, C., Qin, Y., Hao, S.Z. and Yang, D.Z. (2008) Orientation-Dependent Deformation on 316L Stainless Steel Induced by High-Current Pulsed Electron Beam Irradiation. *Materials Science and Engineering*: *A*, **483-484**, 302-305. https://doi.org/10.1016/j.msea.2006.07.179

[9] Hao, S.Z., Wu, P.S., Zou, J.X., Grosdidier, T. and Dong, C. (2007) Microstructure Evolution Occurring in the Modified Surface of 316L Stainless Steel under High Current Pulsed Electron Beam Treatment. *Applied Surface Science*, **253**, 5349-5354. https://doi.org/10.1016/j.apsusc.2006.12.011

[10] Grosdidier, T., Zou, J.X., Stein, N., Boulanger, C., Hao, S.Z. and Dong, C. (2008) Texture Modification, Grain Refinement and Improved Hardness/Corrosion Balance of a FeAl Alloy by Pulsed Electron Beam Surface Treatment in the "Heating Mode". *Scripta Materialia*, **58**, 1058-1061. https://doi.org/10.1016/j.scriptamat.2008.01.052

[11] Guan, Q.F., Wang, X.T., Zhu, J., Chen, K.M., Liang, L., Zhang, Q.Y. and Dong, C. (2009) Fabrication of Micropore on AISI 304L Austenitic Stainless Steel Surface by High-Current Pulsed Electron Beams Irradiation. *ISIJ International*, **49**, 1449-1451. https://doi.org/10.2355/isijinternational.49.1449

[12] Hao, S.Z., Zhang, X.D., Mei, X.X., Grosdidier, T. and Dong, C. (2008) Surface Treatment of DZ4 Directionally Solidified Nickel-Based Superalloy by High Current Pulsed Electron Beam. *Materials Letters*, **62**, 414-417. https://doi.org/10.1016/j.matlet.2007.05.068

[13] Zhang, Z.Q., Yang, S.Z., Lv, P., Li, Y., Wang, X.T., Hou, X.L. and Guan, Q.F. (2014) The Microstructures and Corrosion Properties of Polycrystalline Copper Induced by High-Current Pulsed Electron Beam. *Applied Surface Science*, **294**, 9-14. https://doi.org/10.1016/j.apsusc.2013.12.178

[14] Yablinsky, C.A., Cerreta, E.K., Gray, G.T., Brown, D.W. and Vogel, S.C. (2006) The Effect of Twinning on the Work-Hardening Behavior and Microstructural Evolution of Hafnium. *Metallurgical and Materials Transactions A*, **37**, 1907-1915. https://doi.org/10.1007/s11661-006-0133-8

[15] Norlin, A., Pan, J. and Leygraf, C. (2002) Investigation of Interfacial Capacitance of Pt, Ti and TiN Coated Electrodes by Electrochemical Impedance Spectroscopy. *Biomolecular Engineering*, **19**, 67-71. https://doi.org/10.1016/S1389-0344(02)00013-8

[16] Szummer, A., Janik-Czachor, M. and Hofmann, S. (1993) Discontinuity of the Passivating Film at Nonmetallic Inclusions in Stainless Steels. *Materials Chemistry and Physics*, **34**, 181-183. https://doi.org/10.1016/0254-0584(93)90210-D

[17] Guo, C., Chen, J.M., Yao, R. and Zhou, J. (2012) Microstructure and High Temperature Wear Resistance of Laser Cladding NiCoCrAlY/ZrB_2 Coating. *Rare Metal Materials and Engineering*, **42**, 1547-1551.

[18] Gao, Y.K. (2011) Surface Modification of TA2 Pure Titanium by Low Energy High Current Pulsed Electron Beam Treatments. *Applied Surface Science*, **257**, 7455-7460. https://doi.org/10.1016/j.apsusc.2011.03.005

[19] Gao, Y.K. (2011) Influence of Pulsed Electron Beam Treatment on Microstructure and Properties of TA15 Titanium Alloy. *Applied Surface Science*, **264**, 633-635. https://doi.org/10.1016/j.apsusc.2012.10.083

[20] Walker, J.C., Murrary, J.W., Nie, M., *et al.* (2014) The Effect of Large-Area Pulsed Electron Beam Melting on the Corrosion and Microstructure of a Ti6Al4V Alloy. *Applied Surface Science*, **311**, 345-540. https://doi.org/10.1016/j.apsusc.2014.05.105