

Influence of the pretreatment of the surface on the anodic behavior of zirconium in H_3PO_4 solutions

Anodic behavior was investigated of zirconium in deaerated aqueous H_3PO_4 solutions at room temperatures for mechanically and chemically polished electrodes and for the electrodes cathodically polarized at the potential of $-1,5$ V (SCE). These methods of surface preparation were applied in order to determine their possible influence on anodic behavior of Zr in H_3PO_4 solutions. The investigations were carrying out using potentiodynamic method. The values for the corrosion potentials, corrosion currents and corrosion rates were calculated. These values depend from the surface pretreatment. Chemically polished surface has lowest corrosion rate. The open circuit behavior of zirconium was also investigated. OCP also depends from the surface pretreatment. The structures of the surfaces were study by means of metallography.

Key words: zirconium, pretreatment of the surface, structures of the surfaces, corrosion, OCP

INTRODUCTION

Most engineering metals and alloys oxidize under ambient conditions to form a very thin passive oxide layer, the stability of which in aqueous condition varies with pH and electrode potential [1,2]. Elements such as Zr, Ti and Nb, which belong to a group known as valve metals, usually have their surfaces covered by thin oxide film spontaneously formed in air or in electrolytes at open circuit [3,]. This film constitutes a barrier between metal and medium. Typical value of the initial thickness of these oxide films are in the range 2-5 nm, when formed in air at room temperature [4,5]. Because they are so thin, passive films are difficult to study directly but thicker films of a similar character may be grown by artificially maintaining the high electric field associated with the formation of thin films, so producing anodically formed or anodic films [6,7].

Zirconium is highly reactive, as evidenced by its standard potential of -1.53 V versus the normal hydrogen electrode (NHE) at 25° C. It has a strong affinity for oxygen. In an oxygen-containing medium, such as air, water, or carbon dioxide, zirconium reacts with oxygen at ambient temperature and below to form an adherent, protective oxide film on its surface. This film is self-healing and protects the base metal from chemical and mechanical attack [8,9].

Zirconium alloys exhibit excellent resistance to corrosive attack and works well in many organic and inorganic acids, salt solutions, strong alkalis, and some molten salts. Zirconium's corrosion resistance could be compared with titanium in many ways.

Considering that Zr and its alloys present, among other qualities, excellent mechanical properties, very good corrosion resistance, biocompatibility, and good durability, they become interesting and promising materials for use implants [10-12].

Zirconium anodic oxide films have considerable commercial importance for both corrosion protection and such applications as capacitors and thin windows for electronic devices, radiation counters and radiation sources.

Aim of this work is to determine influence of the pretreatment of the electrode on the anodic behavior of Zr in H_3PO_4 solutions.

EXPERIMENTAL

Electrodes

The working electrode was a rod of polycrystalline (99,2%+Hf) zirconium purchased from Alfa, fixed in a special Teflon holder. The exposed area was $1,2$ cm². The chemical composition of the specimen (wt%) is presented in Table 1.

A platinum wire was used as the cathode. Saturated calomel electrode, (SCE) was used as the reference electrode.

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Table 1 - The chemical composition of the specimen (wt%)

Hf	Fe+Cr	N	O	H	C	Zr
1	0,08	0,005	0,16	0,0003	0,02	balance

Surface preparation

Three different methods of surface preparation were applied in order to determine their possible influence on anodic oxidation.

1. Mechanical polishing

After abrasion with emery paper, the sample was polished on metallurgical cloths with diamond paste of 9 and 3 μm . The polishing with 3 μm diamond paste left a mirror-like surface. The polishing procedure was then continued with 0,5 μm Al_2O_3 to end with 0,05 μm Al_2O_3 for 30 min. Among the different polishing session, the electrode was subject to ultrasonic cleaning.

2. Chemical polishing (etching)

After mechanical polishing, the specimen was immersed 30 s in a solution of 50:47:3 parts by volume triply distilled water, 98% HNO_3 and 48% HF at 0 $^\circ\text{C}$.

3. Cathodic polarization

After mechanical polishing the specimen was cathodically polarized at the potential of -1,5 V (SCE).

Cell and electrolytes

Classical three-electrode cell was used for the measurements. Measurements were performed in $1\text{mol}\cdot\text{dm}^{-3}$ H_3PO_4 . The solutions were prepared from analytical grade chemical and twice distilled water. They were stirred by purified argon.

The equipment

The structures of the surfaces were studied by means of metallography. The metallographic microscope type Neophot 2 was used in the investigations. Electrochemical measurements were carried using HEKA potentiostat/galvanostat.

RESULT AND DISCUSSION

Structural investigation of the initial surfaces

The structure of the surfaces obtained by different pretreatment of the Zr electrode was investigated by means of metallography. Figure 1, 2 and 3 presents the microstructures of the mechanically polished, chemically polished, and cathodically polarized zirconium electrode, respectively.

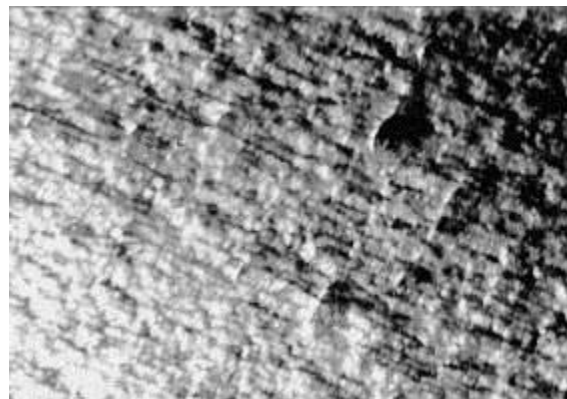


Figure 1 - Microstructure of the mechanically polished Zr surface 200 x

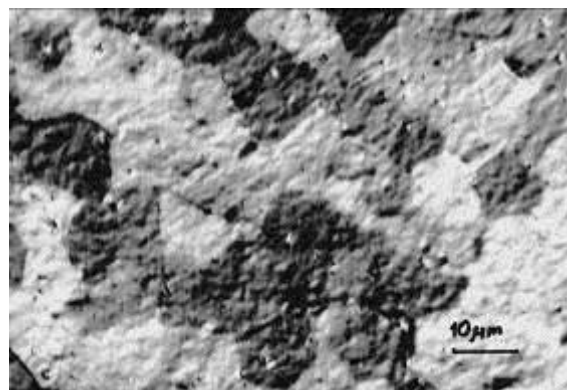


Figure 2 - Microstructure of the chemically polished Zr surface 1000 x

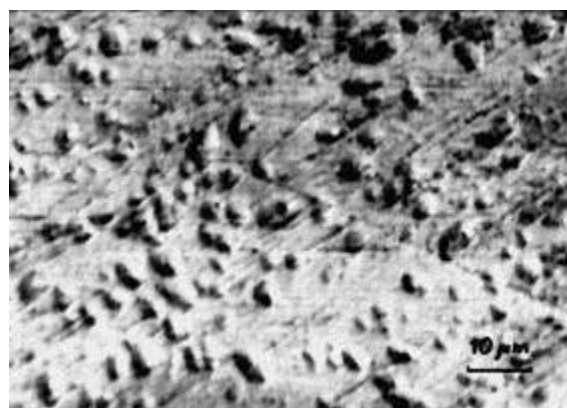


Figure 3 - Microstructure of the cathodically polarized Zr surface 1000 x

Mechanically polished electrode is covered with spontaneously formed oxide film on the surface. The formation of this film begins on the defect places as

result of the polishing, and after that it continuously growth along the all surface. The thickness of the oxide is not equal along the all surface.

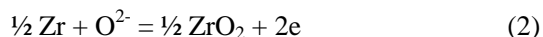
The microstructure of the chemically polished electrode, presented in figure 2 is characterizes with well-defined grains which size is 10-30 μm . As mechanically polished electrode, this electrode is cover with spontaneously formed oxide film, but this film is thinner and it is transparence. Because of the reaction of fluoride ions with Zr, a part of the formed oxide can be soluble.

The chatodic polarization of the electrode was done in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_3\text{PO}_4$ at the potential of -1,5 V (SCE) for the tine of 1 hour. During the chatodic polarization, the spontaneously formed oxide can be reducing. When Zr oxidized in aqueous solutions, it can adsorb part of the liberated hydrogen according these reactions [13].

The water dissociate at the metal surface:



The O^{2-} ions can diffuse across oxide film, and react with Zr on the metal/oxide interface and product electrons:



Low electrical conductivity of ZrO_2 arouse migration of the protons which conductivity is prioritized compared with electronic conductivity, and the $\text{H}_2(\text{g})$ is produced on the metal/oxide interface.



This $\text{H}_2(\text{g})$ can be accumulated on the metal/oxide interface and produce nodules. The number of nodules depended from the polarization time.

OPEN CIRCUIT POTENTIAL

The open circuit potential was measured with respect to SCE in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_3\text{PO}_4$. The variations of the open circuit potential with time for electrodes with different pretreatment are show in figure 4.

The electrodes initially showed a very negative potential that indicative of an active Zr electrode. The open circuit potential gradually becomes more positive, which indicates that the film formation is tacking place. Open circuit potential obtained in our investigations cannot be readily associated with any of the equilibrium reactions presented by Pourbeaux

for the Zr- H_2O system [1]. For example, the potential for reaction 4 at $\text{pH}=0$, -1,553 V (SHE) is considerably more negative than that obtained in our investigations.

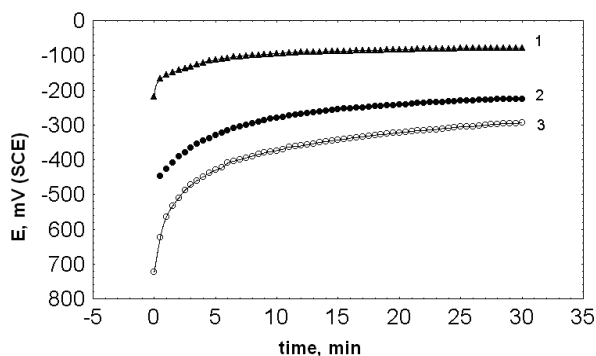


Figure 4 - Variation of the open circuit potential with time for Zr electrodes in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_3\text{PO}_4$ with different pretreatment: 1. chemical polishing 2. chatodic polarization 3. mechanical polishing

This behavior is result of the naturally formed film. This film has a different thickness for the different pretreatment of the electrode. The open circuit potential for chemically polished electrode is more positive than the open circuit potential obtained for the electrode with chatodic polarization and mechanically polished electrode indicates that the spontaneously formed film on this electrode is thinner, than the film formed on the other two electrodes.

ANODIC POLARIZATION

Polarization curves with sufficiently small scan rate can be taking as quasi-stationary state polarization curves. Such are the polarization curves presented in Figure 5 for different pretreated Zr electrodes in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_3\text{PO}_4$ taken at the scan rate $1 \text{ mV}\cdot\text{s}^{-1}$.

Many metals indicate different behavior than that given by Tafel equation. This behavior can be result as a presence of impurities on the metal surface or presence of the oxide film. In these cases, the anodic and cathodic Tafel slops are different from usually. The Tafel slops obtained for Zr in H_3PO_4 with different pretreatment of the electrode have higher values of the slops.

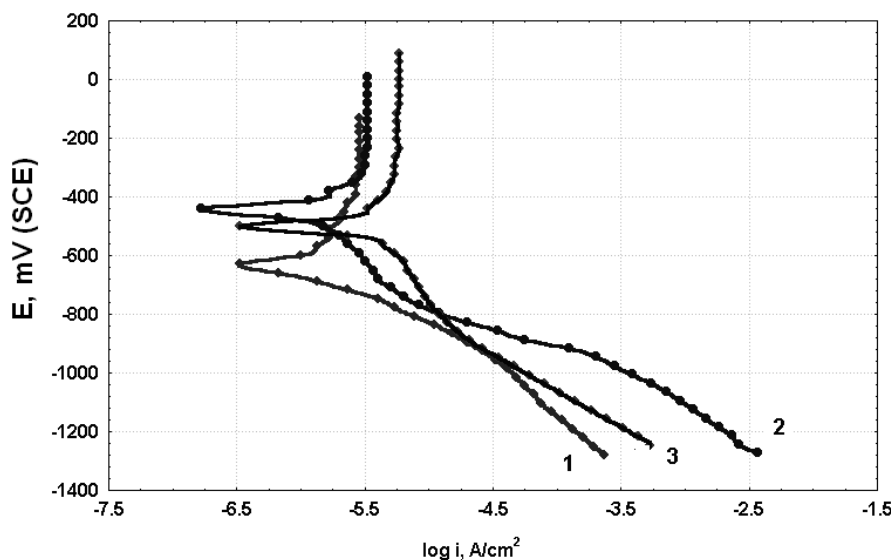


Figure 5 - Anodic polarization curves for Zr electrodes in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_3\text{PO}_4$ $v=1 \text{ mV}\cdot\text{s}^{-1}$:
1. chatodic polarization 2. chemical polishing 3. mechanical polishing

Many metals indicate different behavior than that of zirconium. Higher values of the anodic slope indicate the lower activity of a metal because of the presence of

spontaneously formed oxide. The thickness of this film depended on the pretreatment of the surface as we say before.

Table 2 - Corrosion parameters for the zirconium in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_3\text{PO}_4$

Pretreatments	E_{corr} (V)	I_{corr} (A/cm^2)	β_k (V/dec)	β_a (V/dec)	Corrosion rate (mpy)
Chatodic polarization	-0,52	$3,16\cdot 10^{-7}$	0,161	0,61	0,145
Chemical polishing	-0,44	$2,37\cdot 10^{-7}$	0,14	0,19	0,109
Mechanical polishing	-0,62	$4,16\cdot 10^{-7}$	0,15	0,22	0,191

Table 2 present obtained results. Because the spontaneously formed oxide on the chemically polished electrode is thinner than the oxides formed on the mechanically and for electrode with chatodic pretreatment, the chemically polished electrode has lowest corrosion rate.

CONCLUSIONS

When Zr is exposed to an oxygen-containing environment, an adherent, protective oxide film forms on its surface. This film is formed spontaneously in air or water at room temperature.

The thickness of this film depends on the anodic behavior of zirconium in the H_3PO_4 solutions. Pretreatment of the surface can change the thickness of this film.

The film formed on chemically polished electrode is thinner and transparent.

The film formed on the mechanically polished Zr is thicker, but its thickness is not equal along the all surface.

During the chatodic polarization, the spontaneously formed oxide can be reducing. The $\text{H}_2(\text{g})$ can be produced and can be accumulated on the metal/oxide interface and produce nodules.

The open circuit potential for chemically polished electrode is more positive than the open circuit potential obtained for the electrode with chatodic polarization and mechanically polished electrode.

The corrosion data showed that the surface pretreatment influenced on the anodic behavior of Zr in H_3PO_4 solutions.

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IZVOD

UTICAJ PREDTRETMANA POVRŠINE NA ANODNO PONAŠANJE CIRKONIJUMA U H_3PO_4 RASTVORU

Anodno ponašanje cirkonijuma je ispitano u deaerisanom rastvoru H_3PO_4 na sobnoj temperaturi, pri čemu je elektroda polirana mehanički i hemijski i polarizovana na potencijalu $-1.5V$ (ZKE). Metode pripreme površine elektrode su primenjene u cilju utvrđivanja njihovog mogućeg uticaja na anodno ponašanje Zr u rastvoru H_3PO_4 . Istraživanja su vršena pomoću potenciodinamičke metode. Vrednosti korozionog potencijala, struje korozije i procenta korozije su izračunate. Ove vrednosti zavise od površine predtretmana. Hemijski ispolirana površina elektrode ima najnižu stopu korozije. Otvoreno kolo ponašanja cirkonijuma je, takođe, ispitivano. Potencijal otvorenog kola, takođe, zavisi od predtretmana površine elektrode. Struktura površine elektrode cirkonijuma je ispitivana putem metalografije.

Ključne reči: cirkonijum, pretretman površine, struktura površine, korozija, potencijal otvorenog kola

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