DESIGNING ADVANCED MATERIALS BY ENVIRONMENTAL FRIENDLY PLASMA ELECTROLYTIC OXIDATION

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ABSTRACT

In the CANDU-PHWR nuclear reactors, Zr-2.5Nb coated with a black adherent oxide film of ~1 to 2 $\mu$m in thickness is currently used for the manufacture of pressure tubes. The black oxide thin film has corrosion protective properties. However, it can be damaged during the regular refueling process, thus causing hydrogen/oxygen ingression. Therefore, an enhanced wear and corrosion resistance coating is needed. Plasma electrolytic oxidation (PEO) is an anodic electrochemical treatment, both cost-effective and environmentally friendly, widely used in the formation of a protective oxide film on the metal surface to enhance wear and corrosion resistance as well as prolonging component lifetime. The state of the art reveals that PEO method is suitable for improving the wear resistance of Zr-2.5Nb alloy. Few studies are performed in this field and thus, it is necessary to conduct a more detailed insight study on the processing parameters for PEO treatment. By understanding the influence of process parameters, such as electrolyte temperature and electrolyte composition, we can find the way to obtain a coating with improved mechanical and corrosion properties on zirconium alloys.

Key words: zirconium alloys, black oxide film, plasma electrolytic oxidation (PEO), wear, corrosion resistance

Introduction

Manufactured for the first time in 1957, the pressure tube is a major component of the CANDU reactor. Each pressure tube in a CANDU contains 12 fuel bundles (500 mm long) and heavy water coolant, which is thermally insulated from a low-pressure cooling moderator by a gas annulus formed between the pressure tube and the calandria tube surrounding it [1].
Originally, the reactors used Zircaloy-2. Later, the Zr-2.5Nb alloy was selected to be used because this alloy had a better creep resistance and its higher strength permitted the use of a thinner wall tube with a resultant advantage in neutron economy over Zircaloy-2 in the reactor [3].

The Zr-2.5Nb pressure tubes are heated for 24hr at 400°C in an autoclave to form, on the both inner and outer ring surfaces, a black adherent oxide film of ~1 to 2 μm in thickness [4]. This commercially thin black oxide film has corrosion protective properties. During the refueling process, the oxide film could be damaged, thus causing hydrogen/oxygen ingestion. Therefore, an enhanced wear and corrosion resistance coating is needed.

When an abrupt change it happens in the corrosion resistance, the oxide film, in a relatively short time, changes its color to gray or white and becomes friable and spalling occurs. This change in corrosion resistance is called “transition”. This phenomenon (the “transition”) is characteristic of zirconium and its alloys and limits the life time of the metal. In the nuclear industry, the pressure tubes in CANDU reactors have the life time operation for about 25 years.

Recently, different studies on aluminum, magnesium, titanium and zirconium have been employed in order to increase wear and corrosion resistance.

**Plasma Electrolytic Oxidation**

Plasma electrolytic oxidation (PEO) is a relatively recent surface modification technique providing ceramic coatings with improved corrosion and wear resistance on the metals surface such as aluminum, magnesium, titanium, zirconium and their alloys. This process implies plasma generation in spark discharge channels on the electrode of a metal–electrolyte system under the action of external electric field, chemical reactions between the metal and plasma components, and deposition of the reaction products on the electrode. An additional advantage of the PEO technology is its environmental friendliness and relative low costs [5,6].
The PEO plant

Metal alloys such as aluminum, magnesium, titanium, zirconium can be used as anode material. Rectangular shaped anodes will be placed in electrolytic chamber, see Figure 2, leaving an active surface area. In this example, two platinum wires are used as cathodes. During PEO, the electrolyte is circulated through the chamber-reservoir system (peristaltic pump and heat exchanger) and its temperature is measured in the close vicinity of the anode [7].

PEO is applied above the breakdown voltages of the original oxide films, typically in the range of 400-800 V. For the PEO process can be used various types of power sources including direct current (DC), pulsed DC and alternating current (AC) [5].

The PEO Mechanism

In the coating growth mechanism, discharges play a very important role. In PEO process the discharge events are very short and this makes very difficult to catch them instantaneously to analyze the physical and chemical processes occurring in the discharge channels. Thereby, an existing controversy over the growth mechanism of PEO coatings occurs [9].

The studies show that the PEO coating grows simultaneously above and below the original substrate surface by the combination of two growth mechanisms:

- an outer growth, from the substrate towards the electrolyte, by the melting, oxidation and solidification of ejected species;
- an inner growth into the substrate by an oxygen transport due to the high electric field.
During the inner growth, oxygen anions were transferred into the coating and react with metal cations from the metal substrate to form an oxide ceramic coating. Due to the high cooling rate enforced by the cold substrate, the molten oxide at the coating/substrate interface rapidly solidifies, creating a thin crystalline layer with small uniform nano-sized grains. The nano-crystalline layer is constantly formed during PEO and moves inwards by ‘eating’ the substrate and is considered as the main inner growth mechanism, see Figure 3 [9,10].

**State of the art concerning PEO of Zr-2.5Nb alloy**

Few studies were performed for improving the wear resistance of Zr-2.5Nb alloy. Chen [1] has studied the process of plasma electrolytic oxidation of zirconium alloy Zr-2.5Nb and he has compared the ceramic oxides coatings obtained with the black oxide coating produced commercially. After the rotating mode wear tests, the SEM analysis shows that the PEO coating obtained at small current densities has excellent wear resistance (Fig 4 b). The wear trace on black oxide coating was much wider and deeper and it is clearly seen that all coating material was removed from the substrate (Fig 4 a). Abrasive wear is clearly observed on black oxide coating with wear debris presents in the wear track. For the PEO coating, no obvious abrasive wear and material removal was observed. Thus, the PEO coating had much better wear resistance than the black oxide coating and less wear debris was produced which could lead to contamination of the service environment.

**Fig. 3. Stages of PEO process [8]**

![Stages of PEO process](image)

**Fig. 4** SEM showing wear traces of (a) the commercially black oxide coating and (b) PEO coating [1].
The PEO coating obtained at high current densities showed an improvement of the corrosion resistance of 130 times compared to the uncoated substrate (Zr-2.5Nb), while the commercially black oxide coating is 293 times higher than the substrate. The conclusion was that the commercially black oxide has the best corrosion resistance compared with the PEO coatings obtained until now.

Some prospects for further research work

The factors that affect the PEO processes are: the substrate material, the electrolyte, the temperature, the oxidation time, the electrical parameters, the additives etc. The electrolyte temperature can greatly affect the PEO process. If the temperature is too low, the oxidation process becomes weak, resulting in less thickness and lowers hardness of the PEO coatings. If the temperature is too high, the dissolution of oxide film will be enhanced, and thus cause the coating thickness and hardness to decrease significantly [11]. Therefore, the processing temperature should be studied. Generally, in the PEO process the electrolyte temperature is controlled in the range of 20 - 40°C [11]. But, this is not a rule; this domain depends on the electrolyte - substrate system used first. (K₂Al₂O₄ – Na₃PO₄ – NaOH) – Ti alloy system showed that coatings with more improved wear resistance were obtained at low temperatures (5°C) [12].

The studies of Chen [1] were performed below 60°C. In this context, we consider very important to study the influence of the processing temperature on the coatings properties obtained on Zr-2.5Nb using different electrolytes.

Conclusions

- PEO technique is suitable for improving the wear and corrosion resistances of the zirconium alloys;
- Low current densities increase the wear resistance, while high current densities enhance the corrosion resistance; the black oxide coating has the best corrosion resistance, compared with the coatings obtained until now on Zr-2.5Nb;
- The electrolyte temperature is a critical factor influencing the PEO coating properties; a study about the influence of electrolyte temperature on the formation of PEO coatings on Zr-2.5Nb does not exist.

References


III.2 INTERNATIONAL COOPERATION