Formation of Selective Oxide Layer on FeCrAl Alloy Using Anodization for Nuclear Application

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*Keywords: Structural Materials / Anodization / Selective Oxide Layer / Gen IV Reactor

1. Introduction

Nuclear power plants (NPPs) are well-known for exposing structural materials to harsh environments. These environments cover irradiation effects from highly radioactive species, elevated temperature/pressure conditions, and the presence of corrosive/erosive materials within coolants. These threats pose significant challenges to the durability of materials used to support NPP operations. Moreover, when compared to conventional Pressurized Water Reactors (PWRs) or Boiling Water Reactors (BWRs), next-generation reactors like the Very High Temperature Reactor (VHTR), Molten Salt Reactor (MSR), and Lead or Sodium Cooled Fast Reactor (LFR/SFR) impose even more severe conditions. These advanced reactor environments consist of super high-temperature coolants, highly corrosive atmospheres, and extremely radioactive atmospheres, pushing structural metals and alloys to their limits.

In the aspect of enhancing the durability of structural materials, numerous conventional approaches have been explored. Among these, alloying stands out as a common method to bestow superior properties upon structural materials. However, the development of new alloys is a complex and economically intensive process due to the exhaustive investigative requirements. Similarly, attempts have been made to control the exposed environment, yet managing the intricate array of environments that interact with structural materials proves both arduous and financially demanding.

Within this context, coating techniques emerge as a promising avenue to address these challenges. Extensive research is underway to coat structural materials, thereby augmenting their mechanical and chemical properties. While acknowledged for their efficacy, widely employed methods such as arc ion plating or sputtering suffer from drawbacks including high costs, complexity, and limitations dictated by geometry.

To address these challenges, this study proposes the application of a simple electrochemical technique known as "Anodization" to generate a highly protective oxide layer on target metals. The anodization process comprises oxidation and chemical dissolution processes, the outcomes of which are governed by the respective changes in Gibbs free energy. The oxidation phenomenon's Gibbs free energy change is influenced by the applied potential, whereas the dissolution process is dictated by the chemical composition of the electrolyte employed. By manipulating the extent of oxidation and dissolution processes, it becomes feasible to determine the composition and structure of the resulting oxide layer.

Embracing this theory for oxide layer formation via anodization, the research aims to fabricate a selective oxide layer on alloy surfaces. This entails a deliberate selection of one element from the assortment present in the alloy, which is then subjected to selective oxidation, potentially affording the desired properties.

Consequently, this paper will focus on the fabrication of a selective oxide layer on the FeCrAl alloy. While the current paper concentrates solely on the process of selective oxide layer formation, further characterizations and tests are slated to be conducted to validate its efficacy across diverse nuclear applications.

2. Experimental part

For the anodization process, FeCrAl alloy (Fecralloy foil, Goodfellow) samples were cut into dimensions of 10 x 20 x 1 mm. The composition of the alloy is detailed in Table 1. Before initiating the anodization procedure, the samples underwent electropolishing in a 10-vol% perchloric acid + ethanol electrolyte. This step aimed to ensure the uniform formation of an oxide layer on the surface. Electropolishing was carried out at a voltage of 25 V for 1 min. at a temperature of 20 ℃. Subsequent to electropolishing, the samples were subjected to ethanol sonication for 5 min. for post-cleaning, followed by placement in a 50 ℃ oven.

Table 1. Chemical composition of FeCrAl alloy

FeCrAl alloy:

Fe	Cr	Al	Mn	Si	Y	Zr	C
Bal.	22.0	5.0	0.2	0.3	0.1	0.1	0.02

During the anodization process, measures were taken to mitigate temperature-induced effects on the outcomes, which could impact effective current control. To achieve this, a cooling jacket was employed to maintain the cell temperature at 5 ℃. The counter electrode

utilized a platinum sheet, while electropolished samples served as the working electrode. The spacing between electrodes was set at 20 mm. The electrolyte employed a mixture of Ammonium fluoride (NH_4F) and Potassium Hydroxide (KOH) in Ethylene glycol. The applied potential was then adjusted within the range of 20 – 70 V, with a corresponding duration of 10 – 20 min. Following anodization, the resultant samples were again subjected to sonication in an ethanol bath and subsequently dried in a vacuum oven at 70 ℃.

Morphological characterization of the samples was conducted using a Field Emission Scanning Electron Microscope (FESEM, Hitachi SU5000, Japan) in conjunction with a Focused Ion Beam (FIB, Helios G4, USA). The compositions of the oxide layers were analyzed using Energy Dispersive X-ray Spectroscopy (EDS) attached to the SEM.

3. Results and Discussions

Figure 1 displays the surface morphologies of the bare FeCrAl sample and the electropolished sample. In the case of FeCrAl, precise electropolishing methods were not specified widely. Through experimentation with various conditions, an optimal result was achieved, as depicted in Figure 1. The surface exhibited a considerably smoother texture devoid of discernible defects.
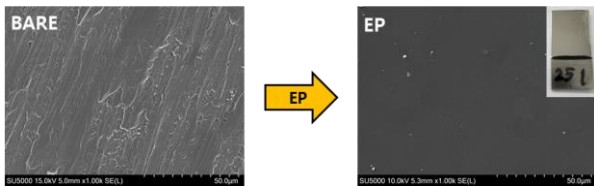

Figure 1. Surface morphology of the electropolished FeCrAl sample

Following the electropolishing process, an anodization process was conducted. Previous research had explored the anodization of Stainless Steel (SS). Given the similar composition of stainless steel to the FeCrAl alloy, an electrolyte comprising 0.1 M NH_4F + 0.1 M H2O + Ethylene glycol was employed for anodization. Applying 80 V to this electrolyte facilitated the formation of a Fe-based oxide layer on the SS due to the higher oxidation potential of Fe compared to Aluminum (Al). Consequently, Al oxidation requires less energy than Fe oxidation. To selectively oxidize Al within the FeCrAl alloy, an initial attempt was made with a lower voltage application. To validate this hypothesis, experiments were conducted with one higher voltage and one lower voltage. Figure 2(a) illustrates the cross-sectional view of the oxide layer produced at 70 V in the 0.1 M NH_4F + 0.1 M H_2O + Ethylene glycol electrolyte. The resultant oxide layer,

akin to SS anodization, primarily comprised Fe (Figure 2(b)). It should be noted that the oxide layer contained a significant fluorine presence due to NH_4F in the electrolyte. Therefore, in this study, the post-heat-treatment procedure at about 500 ℃ for 1 h should be conducted further to fully eliminate the fluorine species and end up with full oxide formation.
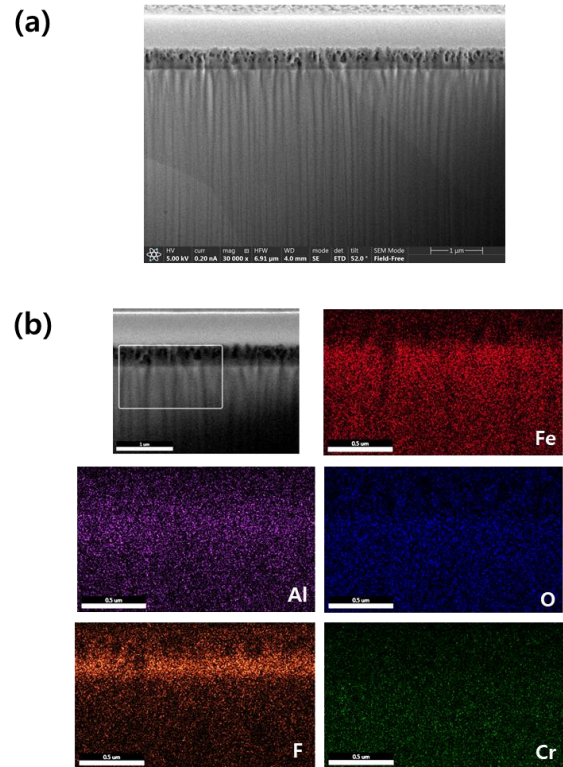

Figure 2. Crossectional morphology (a) and compositional mapping (b) of 70 V anodized FeCrAl sample using NH_4F + H_2O + E.G. electrolyte

At 20 V application, distinct from the earlier condition, predominantly Al oxide was formed, as demonstrated in Figure 3. This observation highlights how control of the applied voltage, representing energy input, enables selective oxidation of specific species.
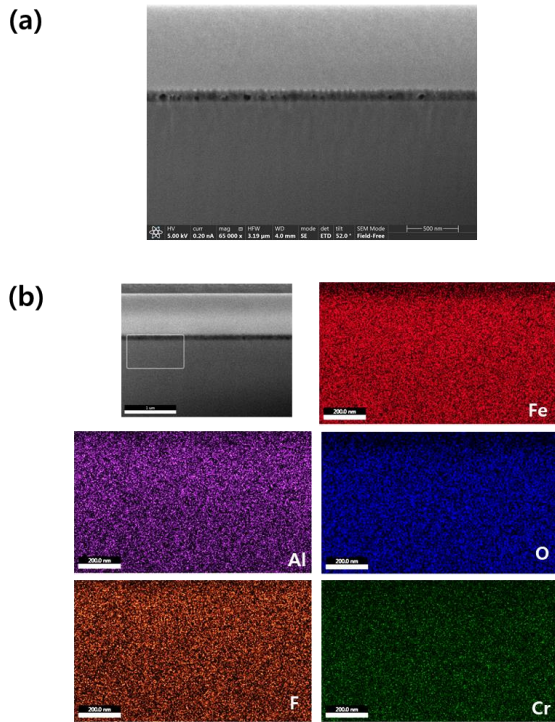
(a)

(b)

Figure 3. Crossectional morphology (a) and compositional mapping (b) of 20 V anodized FeCrAl sample using NH_4F + H_2O + E.G. electrolyte

Figures 2 and 3 both illustrate the porous structure of the oxide layers formed on the surface. While porous oxide layers can offer enhanced stability through the mitigation of volume expansion stress, they may also permit the approach of detrimental particles via the pores. The electrolyte's pH is known to be significant in determining the oxide layer's structure [4]. More acidic electrolytes tend to yield porous oxide layers via anodization, whereas elevating the pH, resulting in a neutral or alkaline electrolyte, tends to reduce pore size or induce the formation of a barrier-type oxide layer (Figure 4). Consequently, anodization was repeated in an electrolyte enriched with KOH. The electrolyte composition comprised 0.1 M KOH + 0.1 M NH_4F + 0.01 M H_2O + Ethylene glycol. Applying a potential of 35 V yielded a substantially more stable barrier-type oxide layer (Figure 5). Composition analysis revealed a predominant Al content within the oxide layer showing the formation of beneficial aluminum oxide layer.
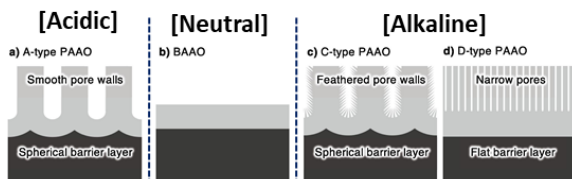

Figure 4. The pH-controlled structural variation of the oxide layer fabricated by the anodization process
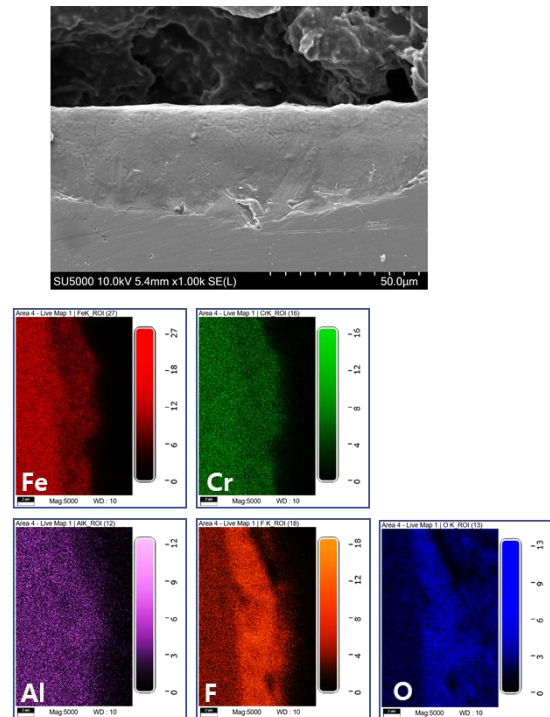

Figure 5. Crossectional morphology (a) and compositional mapping (b) of 35 V anodized FeCrAl sample using KOH + NH_4F + H_2O + E.G. electrolyte

The FeCrAl alloy was developed with the primary intent of forming alumina (Al_2O_3). This compound boasts numerous advantageous properties against harsh environments, rendering FeCrAl alloy suitable for high-temperature conditions where a protective oxide layer is needed. Nevertheless, creating a protective Al_2O_3 (α-phase) layer necessitates exceedingly high temperatures and prolonged durations. Basic requirements entail over 1000 ℃ heat treatment for an entire day, typically conducted in a vacuum or specially treated environment. In comparison, the conditions outlined above present a more straightforward, secure, and cost-effective means of fabricating a selective oxide layer on alloy surfaces. By achieving a selective and advantageous oxide layer, this technique holds promise across various domains of the nuclear industry, addressing a spectrum of challenging conditions.

4. Conclusion

In summary, this study examined the feasibility of achieving selective oxide layer formation through the application of anodization techniques, achieved by precisely controlling both the applied voltage and electrolyte composition. The possibility of this approach was demonstrated using the FeCrAl alloy. Initially, the process was validated by selectively forming oxide layers through voltage manipulation. Lowering the

applied potential led to the oxidation of Al, characterized by its lower oxidation potential, while higher potentials resulted in Fe-oxide formation. Notably, the electrolyte composition delivered a significant influence on the chemical dissolution during anodization. Adjusting the electrolyte composition facilitated the attainment of a more robust and stable form of the selective oxide layer. However, over these results shown above, further characterization should be performed to completely demonstrate the formation of the beneficial barrier layer.

This selective oxide formation technique possesses high promise for utilization in various challenging fields of the nuclear industry, enhancing material stability and lifespan.

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