Potential Use of Ceramic Materials for Supercritical Water-Cooled Reactors

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Abstract

The Supercritical Water-Cooled Reactor (SCWR) presents unique materials challenges due to the effects of corrosion compounded by water radiolysis and materials irradiation. This paper focuses on the general corrosion of ceramic materials (in bulk and coating form) in SCW and surveys the experimental work performed in the area of corrosion and stress corrosion cracking (SCC) of ceramic materials for potential use in a pressure tube SCWR. Among the ceramic materials tested, pure alumina and zirconia/magnesia have so far showed excellent corrosion resistance, while mullite, silicon nitride and silicon carbide based materials showed inferior corrosion resistance compared to the alumina. In addition to the survey, some preliminary test results on several ceramic materials and artificially grown surface oxides will be presented in this paper.

Keywords: Material, Chemistry, Corrosion, Ceramic materials.

1. Introduction

Canada is a member of an international consortium committed to the development of next generation (Gen IV) nuclear power reactors. Six reactor technologies have been selected for research and development under the Gen IV program, Gas Cooled Fast Reactors (GFR), Lead-Cooled Fast Reactors (LFR), Molten Salt Reactors (MSR), Sodium-Cooled Fast Reactors (SFR), Supercritical Water Reactors (SCWR), and Very-High-Temperature Reactors (VHTR). Canada has chosen to focus on a pressure tube SCWR design (Figure 1), as this is a natural evolution of existing CANDU technology. It uses a supercritical light water working fluid loop flowing through pressure tubes enclosed in a deuterium-moderated reactor core. The proposed reactor outlet temperature for the CANDU SCWR may be as high as 650°C [1], at an operating pressure of 25 MPa. The high temperature differential between reactor outlet and inlet enabled by the use of supercritical water allows a high thermodynamic efficiency close to 50%, compared to about 35% for an advanced Light Water Reactor (LWR) [1].

The idea of using supercritical water as a reactor coolant is not new, having originally been proposed in the 1960s. The SCW fossil fuel plant is a mature technology, and state of the art fossil fuel plants can achieve SCW temperatures as high as 610°C [1]. However, a nuclear SCW power plant has unique materials issues due to the closer materials tolerances in the reactor core, the effects of radiation on materials and the coolant, the health consequences of leaks of radioactive materials to the environment.

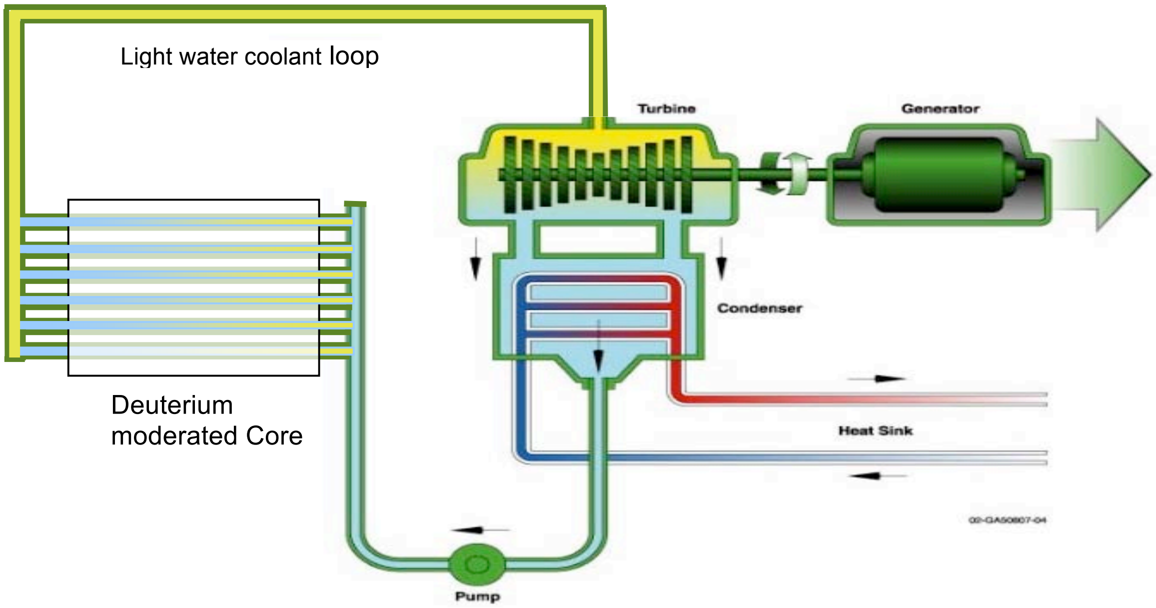

Figure 1 CANDU SCWR [1].

2. Corrosion and Dissolution in Supercritical Water

Water is in the supercritical state at a temperature above 374°C and a pressure above 22.05 MPa. The density and ionic dissociation of water drop significantly at or above the point of transition to the supercritical state. As pressure is increased, the shift in these physical properties becomes more gradual [2]. Figure 2 shows the drop in ionic product and density at pressures of 24 MPa and 38 MPa. The abrupt shift in physical properties affects the corrosion behavior of materials enormously. The point of transition in physical properties rather than the point of transition to the supercritical state more accurately delineates the changes in corrosion characteristics. Water can vary with temperature and pressure from a high density, high polarity solvent to a low density, low polarity solvent.

The performance of materials under SCWR conditions has attracted increased research attention in recent years [3], and some data now exist for about 90 alloys. The critical issues are corrosion, stress corrosion cracking and the effects of irradiation. For the out-of-core SCWR piping, direct irradiation effects are not important, but the dissociation of water by radiolysis in the core may lead to the generation of significant concentrations of hydrogen peroxide and oxygen, which may lead to very oxidizing conditions downstream of the core.

In the proposed CANDU SCWR, water enters the core at a temperature below Tc, and leaves the core at a temperature of up to 650°C, well above the critical temperature. At the core inlet, the water will be a high density polar solvent in which ionic compounds may have high solubility and in which gases have a much lower solubility. At the core outlet, the coolant will be a weak solvent for ionic compounds but a strong solvent for gases. From a corrosion standpoint, there are several distinct sections of the SCWR circuit, each of which will experience a unique corrosion environment.

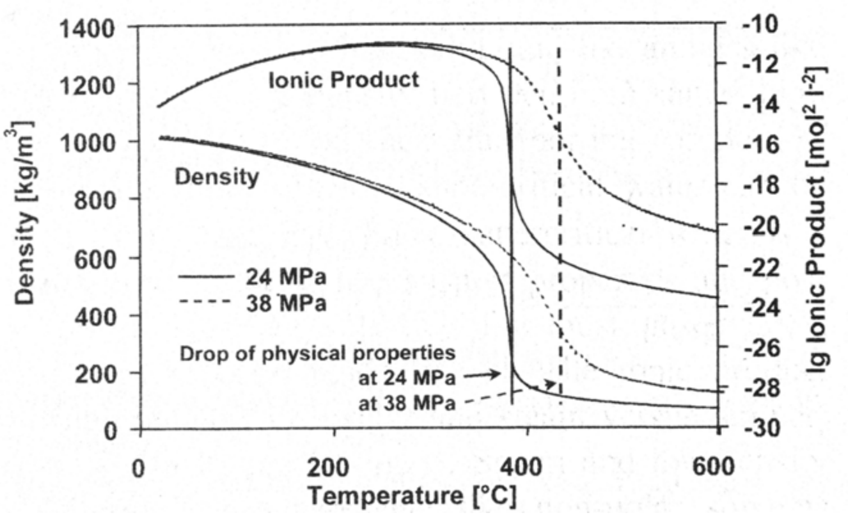

Figure 2 Drop in physical properties of water with temperature [2].

In general, corrosion rates rise with temperature, as reaction rates and diffusion rates increase. However, when the corrosion medium changes state as water does in going from sub-critical to super-critical, a change in the mechanism of the corrosion phenomena occurs. Experiments carried out during the development of supercritical water oxidation processes under acidic, oxidizing conditions at pressures of 24 MPa and 38 MPa [2] showed that the corrosion rate increased enormously at about 320°C regardless of the pressure and the corrosion rate drops to a level comparable to lower temperature values at a temperature that correlates with the density drop of the fluid. Further increase in temperature at higher pressure results in an increase in corrosion rates as the density drop occurs over a broader temperature band.

The reduction in density of water correlates with a drop in ionic solubility. At 25 MPa the dissociation of water peaks at around 300°C with an ionic product concentration that is about 3 orders of magnitude greater than at room temperature. As water transitions to supercritical the reduction in ionic concentrations is about 13 orders of magnitude lower at 500°C than at 300°C. Most metal oxides show increased solubility in either acidic or alkaline solutions, so an increase in the ionic character of water will cause an increase in corrosion. The presence of acids or bases exacerbates the effect.

The solubility of oxygen is an important consideration for an SCWR, as oxygen increases the oxidizing power of the solution. While low concentrations of oxygen (50-300 ppb) have been shown to be beneficial for reducing the corrosion rate of steels in fossil fuel-fired SCW plants, the corrosion rate for many materials nevertheless increases at higher concentrations. Unlike at sub-critical temperatures, in the supercritical state, oxygen is completely miscible with water; in an SCWR, oxygen can be produced in the reactor core by radiolysis. Protective oxide layers like chromia are less stable in these very oxidizing environments due to the formation of hexavalent CrO_4^{2-} (chromate), $HCrO_4^-$, or and H_2CrO_4 (chromic acid) which may dissolve in SCW. A loss of the protective oxide layer will allow attack of the underlying metal.

3. Behaviour of Ceramics in SCW

Various coatings have been considered for use in the primary coolant systems of water-cooled reactors; for example, Kim and Andresen [4] proposed the use of yttria-stabilized zirconia coatings on Boiling Water Reactor piping to minimize intergranular stress corrosion cracking of sensitized stainless steel, by reducing the oxygen transport rate to the surface. Deposition techniques included hydrothermal deposition, plasma spray, and sol-gel methods. Guzonas et al. [5] proposed the use of zirconia coatings, formed by a sol-gel process, on carbon and stainless steels to reduce the corrosion rate in SCW, and Wills et al. [6] examined the use of an atmospheric pressure plasma jet to deposit corrosion-resistant coatings for use in SCW. The stability of ceramics in SCW has recently been reviewed by Sun et al. [7].

AECL has tested a number of ceramics for their stability in SCW, including silicon carbide, magnesia-stabilized alumina, and a number of porous and non-porous yttria-stabilized zirconias. The silicon carbide and magnesia-stabilized alumina samples showed significant weight losses after 500 h of exposure to neutral SCW at 450°C and 25 MPa, while the behavior of the non-porous zirconia samples obtained from different manufacturers varied, with some showing a weight gain and others showing a weight loss after 1100 h exposure to SCW under the same conditions. Samples of high density yttria-stabilized zirconia from two manufacturers showed no detectable weight change after 1100 h (Figure 3), but the samples developed cracks due to thermal shock. A porous, low density yttria-stabilized zirconia showed a slight weight loss in the initial few hours of exposure to neutral SCW at 450°C and 25 MPa, but there were no further weight or dimensional changes after 370 h of additional exposure.

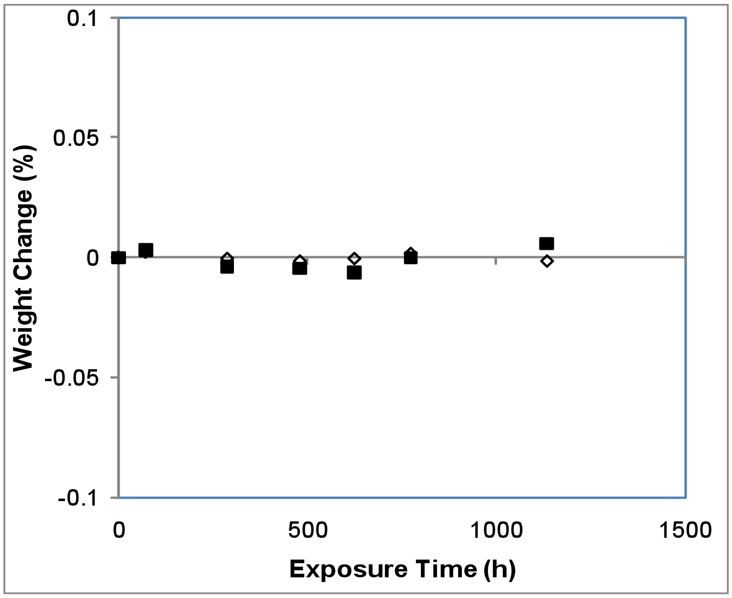

Figure 3 Weight change of yttria-stabilized zirconia as a function of exposure time in SCW at 450°C and 25 MPa. The solid and open symbols are for samples from two different manufacturers.

A broad range of bulk ceramic samples were tested in acidic, oxidizing SCW (465^{O}C, 25 MPa, 3% H_2O_2 and 0.05 mol/kg HCl) during the development of SCWO processes, and the results are summarized in Table 1 [16]. While the acidic test conditions make these results unrepresentative of SCWR chemistry conditions, the data can provide some insight into the degradation of these materials. The pure alumina (Al_2O_3) and sapphire samples showed excellent corrosion resistance, but when zirconia (ZrO_2) was added to alumina the corrosion resistance degraded. The mullite (Al_2O_3/SiO_2) based materials showed inferior corrosion resistance compared to alumina while the yttria stabilized zirconia (YSZ) samples showed very poor corrosion resistance and disintegrated over the duration of the test. Zirconia/magnesia samples were found to be very corrosion resistant in that they exhibited no mass loss, but the HIPPed (hot isostatically pressed) sample cracked due to crystal structure changes. The original sample contained 30% tetragonal ZrO_2, which transformed to monoclinic ZrO_2 during the test, causing volume expansion and subsequent cracking [16]. It is to be noted that YSZ behaved differently in SCW (Figure 3) and SCWO (Table 1) due to the nature of water chemistry; the supercritical water contained less than 1 ppm dissolved oxygen while the SCWO test used water with 3% H_2O_2.

Table 1 Corrosion performance of various ceramics in SCW at 465^{O}C and 25 MPa [16]

Material	**Exposure time (h)**	**Corrosion rate (mg/cm^2)**	**Corroded layer (µm)**
Sapphire	144	<0.1	<10
99.7% Al_2O_3	220	<0.1	<10
90% Al_2O_3, 10% ZrO_2	143	0.33	1150-1350
80% Al_2O_3, 18% ZrO_2	143	0.79	230-260
Al_2O_3, ZrO_2, 3% Y_2O_3	133	0.31	310
72% Al_2O_3, 8% ZrO_2, 20% TiC/TiN	150	5.25	<10
60% mullite, 40% ZrO_2	144	0.27	<10
60% mullite, 10% Al_2O_3, 30% ZrO_2	133	1.76	500-600
70% mullite, 10% SiC, 15% ZrO_2, 5% Al_2O_3	144	2.28	170-220
50% mullite, 40% SiC, 10% ZrO_2	133	13.09	350-500
97 mol% ZrO_2, 3 mol% Y_2O_3	9	disintegrated	
89.5% ZrO_2, 10.5% Y_2O_3	140	disintegrated	
96.5 mol% ZrO_2, 3.5 mol% MgO	220	<0.1	<10
92.1 mol% ZrO_2, 7.1 mol% MgO, 0.8 mol% Y_2O_3 + 3 vol% spinel	144	0.36	<10
91.7 mol% ZrO_2, 7.8 mol% MgO, 0.5 mol% Y_2O_3 + 3 vol% spinel	140	-0.76 (weight gain)	<10

Material	Exposure time (h)	Corrosion rate (mg/cm^2)	Corroded layer (μm)
> 99% Si_3N_4, free Si <1%	144	129.49	<10
93% Si_3N_4, 5% Y_2O_3, 2% Al_2O_3	150	51.93	<10
> 79% Si_3N_4, 20% SiC platelets, free Si <1%	135	61.36	<10
> 74% Si_3N_4, 19% SiC platelets, 5% Y_2O_3, 2% Al_2O_3	143	55.69	<10
Si_3N_4 - TiC/TiN	143	59.81	300
β-Sialon, $Si_{5.3}Al_{0.7}O_{0.7}N_{0.7}$	150	74.19	400
S-SiC	133	75	
99% SiC, 1% Al_2O_3	150	33.93	<10
AlN	80	-4.83 (weight gain)	
B_4C, BN,TiB_2, Y_2O_3	80	disintegrated	

Si_3N_4 and SiC based materials all showed poor corrosion resistance, but the addition of 1% Al_2O_3 to SiC reduced its corrosion rate by more than 50%. All other ceramic materials, including boron carbide, boron nitride, titanium boride, and yttria, showed poor corrosion resistance and disintegrated over the duration of the test. The one exception was aluminum nitride, which showed a weight gain during the test because the Al transformed to a protective Al_2O_3 layer [16].

The poor corrosion performance of SiC coatings was corroborated in other work where CVD SiC coatings were tested in SCW at 25 MPa and 500°C (deoxygenated water with 25 ppb DO). The corrosion rates for the CVD SiC was lower than that previously measured for reaction bonded and sintered SiC, but substantial corrosion was evident after 21 days of exposure. Surface pitting to a depth of 5 μm was observed (≈10% of film thickness). The SiC coating was preferentially attacked at grain boundaries, but for the duration of the test no significant loss of surface grains occurred [17].

4. Oxide Forming Metallic Coatings

Most ceramic materials have poor manufacturability (shaping or welding, for example) and damage tolerance and are therefore not suitable for load-carrying applications. In-situ formation of oxides on the surface of metallic component offers the advantages of structural capability and corrosion resistance. The primary constituents for oxidation resistance in nickel-base alloys and stainless steels are chromium and aluminum. Chromium forms chromia (Cr_2O_3), which is a very adherent protective scale, while aluminum forms alumina (Al_2O_3), which is also a very adherent protective scale. The presence of chromium further promotes the formation of the protective alumina scale [18].

Various Al and/or Cr containing metallic coatings have been applied to steel substrates for corrosion and oxidation resistance. Hot-dipped aluminum on 9Cr-1Mo steel (SA213 T9) [19] and plain low carbon steel [20] encouraged an Al_2O_3 surface scale formation upon thermal exposure. However, further thermal exposure led to cracking and spalling of the coatings [21]; this observation strongly suggests that simple hot-dipped aluminum coatings are not suitable for SCWR applications. On the other hand, the pack cementation process of applying an aluminum coating to Inconel 625 [22] also resulted in the formation of Al_2O_3 surface layer and the coating showed better spallation resistance than the hot-dipped aluminum coatings on steels.

MCrAlY (where M is typically Fe, Ni, Co, or a combination of these) coatings are an industry standard coating which have shown superior oxidation and corrosion resistance in extreme environments such as gas turbine engine components. The oxidation resistance is afforded by surface layers of alumina and chromia. The presence of chromium increases the activity of aluminum such that alumina is more readily formed. The reactive element yttria assists in bonding the coating through the formation of acicular peg-like grains which serve to anchor the coating. While FeCrAlY was one of the originally developed MCrAlY coatings [23], it showed poorer stability than NiCrAlY based coatings. Since cobalt release into the coolant can led to the formation of ^{60}Co by neutron activation, leading to high radiation fields around system piping, the candidate alloy systems should contaion no cobalt. For these reasons, we have focused our effort on the development of NiCrAlY based coatings.

In addition to Al and Cr containing materials, Ti alloy was also considered. While there have been limited studies on the behavior of Ti alloys in SCW, one study showed that some of the β Ti alloys had a similar corrosion resistance as stainless steels 316LC and 304 [24]. Although Ti alloys lose their strength at temperatures over 550°C, for applications at lower temperatures Ti alloys offer advantages in terms good corrosion resistance, improved weldability and formability. Additionally, TiO_2 surface layer can be readily formed using either anodizing or heat treatment.

5. Recent Experimental Work on Artificial Formation of TiO_2, Cr_2O_3 and Al_2O_3

To examine the potential of artificially grown oxides in protecting substrate materials from excessive corrosion in SCW environment, three types of thermally grown oxides were obtained and tested at 470°C and 24 MPa for a total duration of 425 hrs. The three substrate materials selected were Hastelloy X, NiCrAlY and commercially pure titanium (CP-Ti). Heat treatment was conducted in an air furnace to generate dense thermally grown oxides (TGO) (chromia, alumina and titania, respectively) on the three substrates. The oxide films formed are shown in Figures 4, 5, and 6. The compositions of the TGO films were determined using EDS which showed substantial oxygen and Cr, Al or Ti. An example of the EDS analysis of alumina is given in Figure 7. Although chromia is known to be volatile under oxidizing environment above 850°C, the effect of Cr containing TGO was examined this research since the intended service temperature for these coatings falls below 850°C [25].

After oxide formation, the samples were tested in SCW along with freshly polished samples of untreated substrates to compare the weight and microstructure changes. The results revealed that the heat treated Hastelloy X had a 50% reduction in weight loss comparing to that of the polished Hastelloy X. The heat treated NiCrAlY sample showed a slight weight loss (0.042%) while the polished NiCrAlY showed a weight gain. Lastly, the weight loss was reduced by 30% in CP-Ti sample with thermally grown TiO_2 when compared to polished CP-Ti sample.

A detailed study of the microstructure of the SCW-exposed samples is in progress and the results obtained so far are very encouraging.

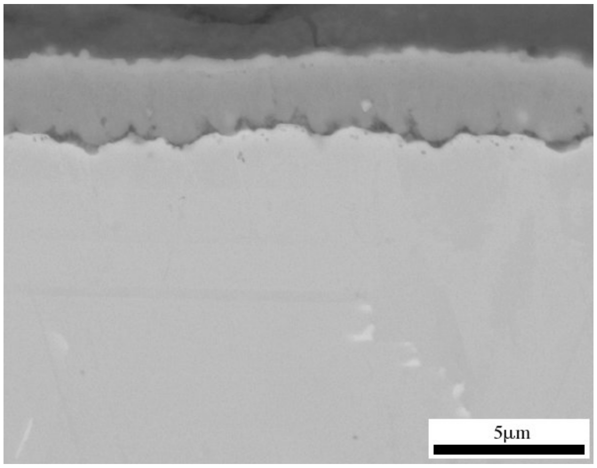

Figure 4 Formation of chromia on hastelloy X after heat treatment.

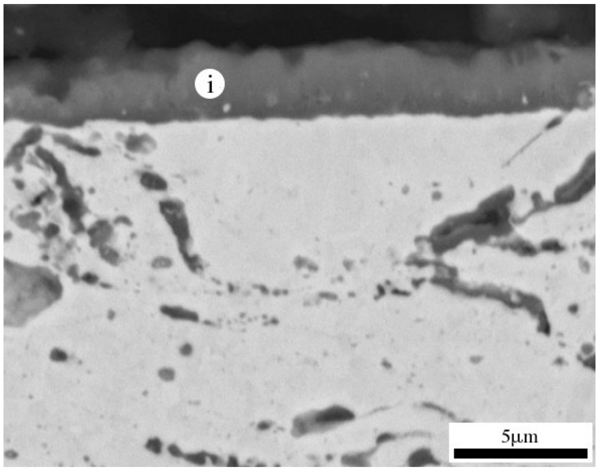

Figure 5 Formation of alumina on NiCrAlY after heat treatment.

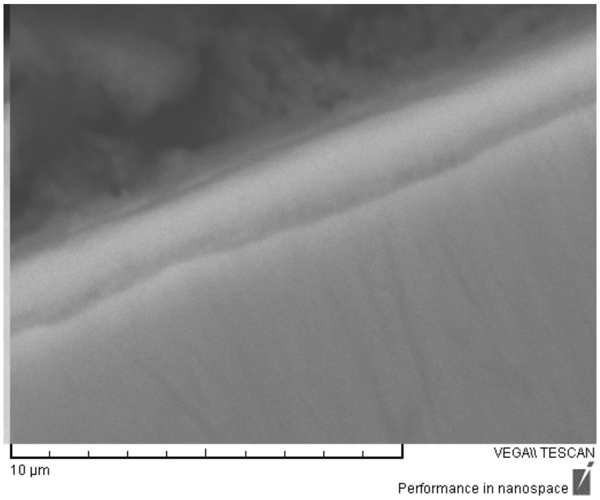

Figure 6 Formation of TiO_2 layer on CP-Ti after heat treatment (oxide thickness: 1.5 µm).

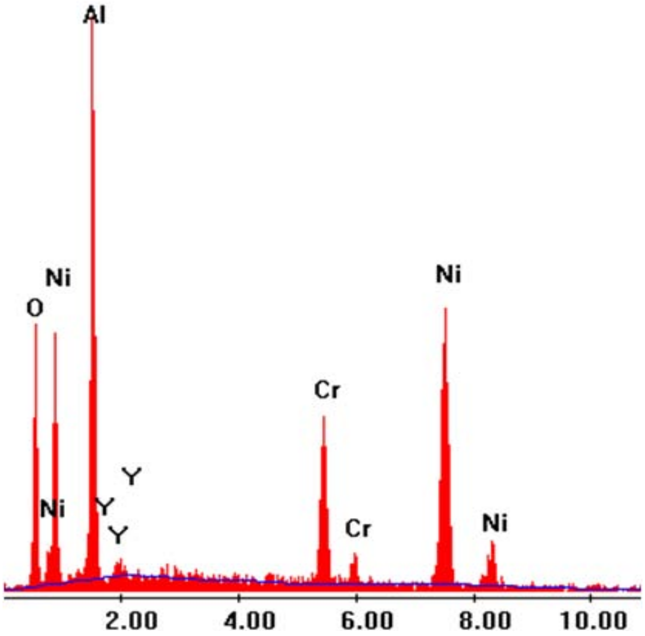

Figure 7 EDS spectrum of alumina layered formed on NiCrAlY.

6. Conclusion and Future Work

From the results on the ceramics sample tests, alumina showed promise as an oxidation resistant coating for an SCW environment. Preliminary test in this research also indicated that chromia and titania could also offer corrosion resistance for applications in the low temperature regime within the reactor. The most severe corrosion environment is likely to be high temperature subcritical water, therefore, the tests are being carried out to include subcritical water corrosion tests. The test specimens are being designed to have residual tensile stress in order to evaluate the tendency for stress corrosion cracking of the potential substrate and coating materials.

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