Effect of Cr/Al ratio on the development of oxidation properties of protective coating

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1. Introduction

Zirconium and its alloys are extensively are used as nuclear energy materials owing to their low neutron capture cross sections, high mechanical strength, creep resistance, and corrosion resistance in boiling water and steam environment. The major application of zirconium alloys both in PWR and BWR type reactors is fuel cladding tubes which enclose nuclear fuel and emit neutrons into coolant neutrons into coolant water which hats up and transfers energy from the reactor [1]. However, zirconium and its alloys have poor oxidation resistance especially at elevated temperature, because zirconium allooys react with water, releasing a large amount of hydrogen gas and heat above 1473 K.

Since the Fukushima accident, the safety of nuclear reactor has become one of the major concern. Therfore, Accident tolerant fuel (ATF) claddings have been widely studied. As a short-term solution for the development of ATF, a coating technology for the fuel cladding surface has been considered to decrease the high-temperature oxidation rate of zirconium-based alloy. Recently, Terrani et al. reported the oxidation resistance of Fe-based alloys for protecting zirconium alloys from the rapid oxidation in a high-temperature steam environment [2]. Kim and co-workers also reported the corrosion behavior of Cr-coated zirconium alloy using a plasma spray and laser beam scanning [3]. Park et al. also reported the corrosion behavior of Cr-coated Zircaloy-4 [4].

In this paper, we coated Zircaloy-4 claddings with Cr-alloy at different Al concentration using cathodic arc ion plating (CAIP) and their corrosion behavior in high temperature and steam environment was also investigated.

2. Methods and Results

2.1 Coating procedure

CAIP is the coating technology to improve the adhesion owing to good throwing power, and a dense deposit [5]. Thus, considering the advantages of CAIP, It is a promising method for depositing oxidation-resistant coating on nuclear fuel claddings.

Cr-alloy coatings were deposited on the Zircaloy-4 using the CAIP with Cr/Al target. The Zircaloy-4 claddings were cleaned ultrasonically in ethanol and acetone solution, and the Zircaloy-4 claddings were then mounted in a vacuum chamber. The chamber was evacuated to a pressure of 1 x 10^{-5} Torr, and heated simultaneously to 473 K to eliminate the residual gas adsorbed on the chamber wall and substrates. Prior to the deposition, the substrates were sputter cleaned using Ar^+ ions under -500V negative bias voltage for 5 min. Ion bombardment was applied to remove contaminants and ensure good adhesion of deposited coatings. The deposition of Cr-alloy was carried out in an Ar atmosphere with a pressure of 5mTorr. The samples were negatively biased at 150 V during the deposition. After deposition, the coatings were polished to reduce the influence of the roughness, as well as for more precise measurements. Fig. 1 shows a photograph of the coated cladding by CAIP.

Fig. 1. Cr-alloy coated Zircaloy-4 by CAIP.

2.2 Evaluation of coating characteristics

The thickness and microstructure of the coatings were observed using a scanning electron microscope (SEM, JEOL, JSM6300, 20kV) equipped with an energy dispersion spectrometer (EDS). Fig. 2 shows the cross-sectional SEM image of the Cr-alloy coated Zircaloy-4 cladding. . The thickness of a Cr-alloy layer is about 40 μm, and the Cr-alloy coating shows dense microstructure with a well-defined interface.

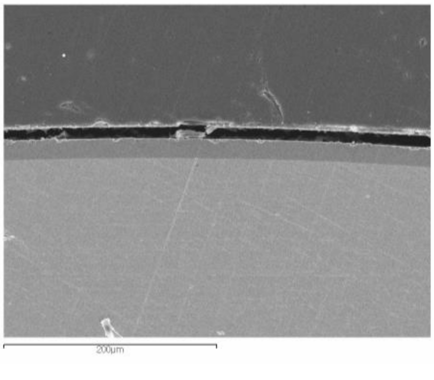
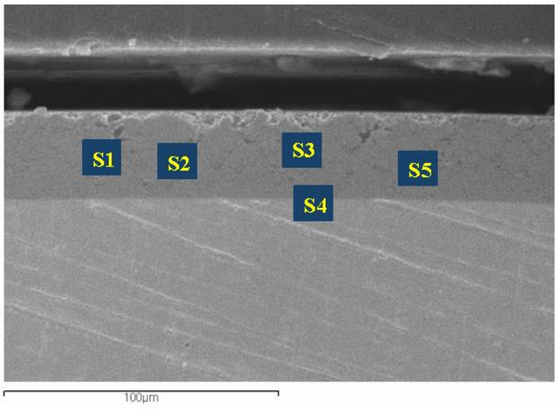
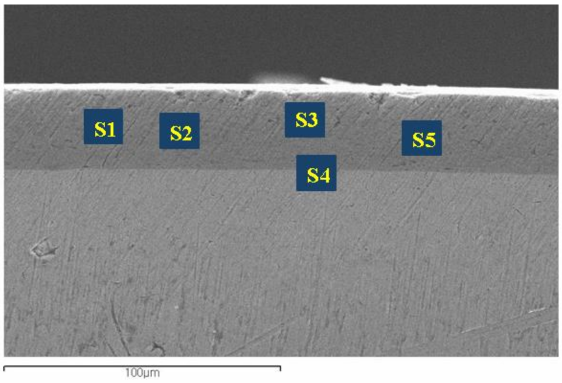


Fig. 2. SEM image of the Cr-alloy coated Zircaloy-4 by CAIP

The chemical compositions for the deposited film were characterized by EDX, and the results are show in Fig. 3. The compositions of the films were estimated to be 70wt%Cr-30wt%Al and 85wt%Cr-15wt%Al.



Spectrum	Al	Cr	Zr	O	Total
S 1	31.17	67.31	0.87	0.65	100.00
S2	30.85	67.97	0.67	0.51	100.00
S3	28.46	69.41	1.29	0.84	100.00
S4	30.94	65.83	2.46	0.77	100.00
S5	28.19	69.59	1.37	0.85	100.00



Spectrum	Al	Cr	Zr	O	Total
S 1	13.87	84.79	0.86	0.48	100.00
S2	16.24	82.91	0.32	0.53	100.00
S3	15.58	83.44	0.64	0.34	100.00
S4	13.78	84.82	1.27	0.13	100.00
S5	12.98	85.41	0.98	0.63	100.00

Fig. 3. EDX results of Cr-alloy film

To investigate the effect of a protective Cr-alloy layer on the high-temperature oxidation behavior of Zircaloy-4, the high-temperature oxidation tests were performed in a 1473K steam environment using a thermo-gravimetric analyzer (TGA) for up to 2000 s (Fig. 4).

The weight gains of the tested samples are shown in Fig. 5. The Cr-alloy (85wt%Cr-15wt%Al) film showed excellent oxidation resistance compared to the Cr-alloy (70wt%Cr-30wt%Al) film. The microstructures of coated samples after oxidation will be investigated.

3. Conclusions

In this study, the dense and homogeneous Cr-alloy films were successfully deposited on the Zircaloy-4 claddings by the CAIP system and the influence of Al concentrations on the corrosion property was studied through high-temperature steam oxidation test. The 85wt%Cr-15wt%Al coating is a promising candidate for ATF claddings.

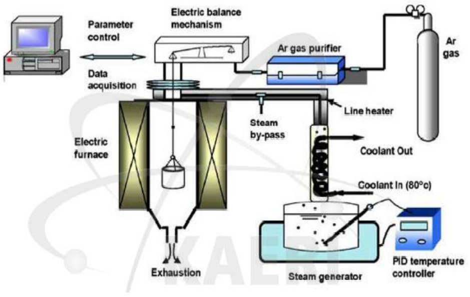


Fig. 4. Schematic of high-temperature steam oxidation test apparatus.

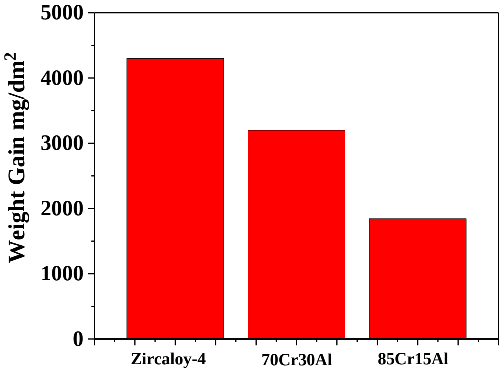


Fig. 5. Corrosion behaviors of the Cr-alloy coated Zircaloy-4 with different Al concentration.

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