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**A COMPARISON OF TWO ALUMINIZING METHODS
FOR CORROSION PROTECTION IN THE WET SEAL OF
MOLTEN CARBONATE FUEL CELLS***

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During testing, the cell potential was maintained at 800 mV at 650°C for 500 h. After the test, the samples were cleaned with dilute acetic acid and mounted for metallography.

Scanning-electron microscopy (SEM) analyses were performed to characterize the microstructure of each coupon. Energy dispersive analysis of X-rays (EDX) was used to assess the interdiffusion of the steel and aluminizing layers. The compositions were calculated from the observed ratio of the metals. X-ray diffraction (XRD) was used to identify the phases present on, and immediately below, the surface of the sample.

RESULTS AND DISCUSSION

As-received Coupons

A serrated microstructure was seen at the Al/SS interface in both types of samples (see Fig. 2). The thickness of the interfacial layer was about 1.5–3.0 μm .

The microstructure of set 1 samples consisted of a duplex structure on the SS base metal. Analyses by XRD showed that the outer layer consisted of Al and the inner layer consisted of iron aluminides. The EDX and XRD analyses showed that the bulk of the inner layer consisted of Fe_2Al_5 ; FeAl_3 was found near the Al/SS interface (Fig. 3).

The microstructure of set 2 samples consisted of a single layer of iron aluminides. The EDX analysis showed that the bulk of the layer consisted of FeAl_3 ; FeAl_2 was present at the Al/SS interface. The different phase distribution between sets 1 and 2 is due to the differences in the aluminizing process.

During the aluminizing process, Cr and Ni also diffuse into the aluminizing layer.¹⁰ As expected, the concentrations of these species are greatest at the interface. For example, the concentrations are 8 and 10 wt% for Ni and Cr, respectively, in the set 2 samples. No aluminum was found in the SS substrate.

In-cell Test

After 500 h of in-cell testing, different intermetallic phases were seen metallographically between the two sets of coupons. No microstructural differences were seen between the samples from the fuel gas inlet and gas outlet. The EDX analyses of set 1 coupons revealed the following intermetallic phases: FeAl , FeAl_2 , Fe_3Al , and Fe_2Al_5 (see Fig. 4). Similar analyses of set 2 coupons revealed only FeAl and FeAl_2 .

The set 1 samples did not show significant corrosion after the test. The thickness of the aluminum layer remained unchanged and no noticeable corrosion scale developed. A closer examination of these samples showed a rough surface (Fig. 4). The surface texture was first thought to be from the aluminizing process. In the thermal-spray process, aluminum droplets strike the surface of the steel, producing a rough texture due to droplet splattering. Samples of set 2 showed a similar phenomenon, that is, a rough texture on the outer surface of the aluminizing layer (Figs. 5a and 5b). However, the slurry-coating process produces a smooth surface; thus, the observed texture cannot be from the set 2 aluminizing process. The texture of the set 2 sample goes farther into the deposit than that of the set 1 sample: it penetrates a distance of 15–25 μm .

The EDX results from the regions near the electrolyte of set 1 and set 2 samples show that the atomic ratios of the metals are different. The ratio of $\text{Fe}:\text{Al}:\text{Cr}:\text{Ni}$ is 2.3:10:1:1 for set 1 and 3.5:5:1:1 for set 2. The high Fe concentration in set 2 is expected

because its bulk composition began the experiment as FeAl_3 . The high Fe concentration in the aluminizing layer may be the cause of the greater corrosion damage in set 2 coupons.

The phase distributions are different in the two types of coupons, as shown by XRD (see Figs. 6a and 6b for sets 1 and 2, respectively). The phases present in both samples are α - and γ - LiAlO_2 , Cr_4Al_9 , Fe_2Al_5 , FeAl or Fe_3Al ,¹ and an unknown phase. The ratio of the phases was calculated using the intensity of the diffraction peaks at $2\theta = 18.7, 22.5, 43.2, 42.8$, and 44.1° , respectively. These ratios are given in Table 1 and indicate which species provide corrosion protection.

Table 1. Intensity Ratios of Species in the Set 1 and Set 2 Aluminizing Layers

	Intensity Ratio		
	α - γ - LiAlO_2	$\text{Fe}_2\text{Al}_5:\text{Cr}_4\text{Al}_9$	$\text{FeAl}^2:\text{Cr}_4\text{Al}_9$
Set 1	0.7	0.6	0.3
Set 2	2.0	2.7	14.7

² FeAl and/or Fe_3Al .

Initially, the electrolyte tile consisted of γ - LiAlO_2 + $(\text{Li},\text{K})_2\text{CO}_3$. The greater amount of α - LiAlO_2 on set 2 samples as compared to that on set 1 samples indicates greater oxidation of the aluminizing layer. However, a corresponding Fe-containing product from the reaction was not observed (e.g., LiFeO_2). An explanation is that the Fe-containing product spalled off or came off during the acetic acid cleaning.

We found that the lithium aluminates are easily removed by soaking the sample in 50% nitric acid for about 1 minute (XRD evidence). Thus, the lithium aluminates are present on the surface and are not tenacious; the other peaks present in the XRD before the washing are still there afterwards.

The high concentration of Fe-containing phases present in set 2 is more important than the presence of lithium aluminates. As stated earlier, the bulk of set 2 coating material initially consisted of FeAl_3 . The distribution of phases shown in Table 1 indicates the equilibrium composition of FeAl_3 and Type 310S SS. Since the $\text{FeAl}/\text{FeAl}_3$ -type materials predominate, they may be responsible for the corrosion behavior of the set 2 material. Separate experiments on the corrosion behavior of the Fe- and Cr-containing phases given in Table 1 are necessary to determine which is the most corrosion resistant (i.e., protective) coating material.

CONCLUSIONS

Examination of set 1 and 2 samples reveals an initially serrated interface that consists of iron aluminides. Resolvable, changes in the bulk microstructure occurred after about 500 h. No corrosion layer growth was observed, but some of the aluminum deposit formed Fe-Al phases in both coupons.

¹The XRD patterns of FeAl and Fe_3Al are too similar to be differentiated here. The exact patterns are found on JCPDS Card Numbers 33-0020 and 45-1203, respectively.

Interfacial Zone

Fig. 2. Typical serrated layer found at the Al/SS interface of all as-received samples. This micrograph is from a set 2 coupon before exposure.

Fig. 4. Micrograph of aluminizing layer on a set 1 coupon after 500 h of in-cell test. Air was the cover gas; sample was placed in the fuel exhaust section of wet seal.

Fig. 3. Micrograph of Al/SS interface of a set 1 coupon before in-cell test showing the locations of the spot analyses.

Fig. 5a. Micrograph of aluminizing layer on a set 2 coupon after 500 h of in-cell test. Air was the cover gas; sample was placed in the anode exhaust section of the wet seal.