Looking to the future PATRAM 2010

ACCELERATED CORROSION TESTING OF ALUMINUM BORON CARBIDE METAL MATRIX COMPOSITE IN SIMULATED PWR SPENT FUEL POOL SOLUTION

Daisuke Nagasawa
Nippon Light Metal Company, Limited
1-34-1 Kambara, Shimizu-ku, Shizuoka-shi, Shizuoka-ken, JAPAN

Valentin Rohr
AREVA TN International
1 rue des hérons, 78180 Montigny le Bretonneux, FRANCE

Hervé Issard
AREVA TN International
1 rue des hérons, 78180 Montigny le Bretonneux, FRANCE

Hideki Ishii
Nippon Light Metal Co., Ltd.
1-34-1 Kambara, Shimizu-ku, Shizuoka-shi, Shizuoka-ken, JAPAN

Kazuto Sanada
Nippon Light Metal Co., Ltd.
2-2-20 Higashi-Shinagawa, Shinagawa-ku, Tokyo, JAPAN

ABSTRACT
The MAXUS® Al/B_4C MMC plate has been developed by Nippon Light Metal as a neutron absorber for basket plates in both dry storage casks and wet storage racks. The material's relatively low weight, high thermal conductivity, high mechanical strength and other properties makes it attractive for both applications. If MAXUS® is to be used as neutron absorber for storage racks immersed in spent fuel pools, the MMC must maintain its stability during long-term exposure to the pool environment. In order to investigate the long-term stability of the MAXUS® Al/B_4C MMC plate for use in wet storage racks, accelerated corrosion testing has been performed with a simulated PWR spent fuel pool solution for 10,080 hours. The MAXUS® plate is produced using a powder metallurgy process and has a sandwich structure with Al/B_4C MMC core and thin aluminum skins. Samples for corrosion testing were cut from plates having a 15 wt%-B_4C core. Corrosion testing of anodized and non-anodized samples was performed at 363 K in accordance with ASTM G31-72 (2004) [1]. After the accelerated corrosion testing, the aluminum surface cladding and its anodic film were slightly hydrated; however, all coupons had no blisters, swelling or other abnormalities that cause loss of boron carbide. The metal loss measured by corrosion weight loss after removal of the aluminum hydrate layer is small and it is not considered to be significant for practical use. Because the metal loss shows no difference between 4,320 hours and 10,080 hours, it can be considered that the hydration reaction with solution has stopped after 4,320 hours. These results confirm that MAXUS® has good corrosion resistance in the simulated PWR spent fuel pool solution.

INTRODUCTION
The MAXUS® Al/B_4C MMC plate has been developed as a neutron absorber for basket plates in both dry storage casks and wet storage racks. In order to investigate the long-term stability of the MAXUS® Al/B_4C MMC plate for use in wet storage racks, accelerated corrosion testing was performed.

EXPERIMENTAL PROCEDURES
Accelerated corrosion testing was performed with a simulated PWR spent fuel pool solution (including 3000 mg/kg boron as boric acid) for 10,080 hours. Coupons for corrosion testing (size: 50 mm x 100 mm x 2 mm) were cut from plates having a core of 15 wt%-B_4C and skins of about

190 μm in thickness. Corrosion testing of anodized and non-anodized coupons has been performed at 363 K in accordance with ASTM G31-72 (2004) [1]. Table 1 shows the testing conditions. Coupon #5 and #6 were anodized with a sulfuric acid solution and pores of the anodic films were sealed after anodizing. The anodic films of the core at the edges of the coupons were thinner than that of the skin because of the influence of the B_4C particles.

Table 1. Testing Conditions

Coupon #	Surface Treatment	Thickness of the Anodic Films	Immersion Period	Cell #
1	non-Anodized	-	4,320 h	A
2	non-Anodized	-	4,320 h	
3	non-Anodized	-	10,080 h	B
4	non-Anodized	-	10,080 h	
5	Anodized	Skin: 4-5 μm Core: 2-3 μm	10,080 h	C
6	Anodized	Skin: 4-5 μm Core: 2-3 μm	10,080 h	
-	(Blank Test)	-	10,080 h	D

RESULTS

Water Chemistry

Figure 1 shows the conductivity and pH of the bath. The pH hardly changed though the conductivity increased a little. Sulfuric acid ion was detected from the bath in cell C, and there is a high probability that this sulfuric ion dissolved from anodic films caused the increase of the conductivity.

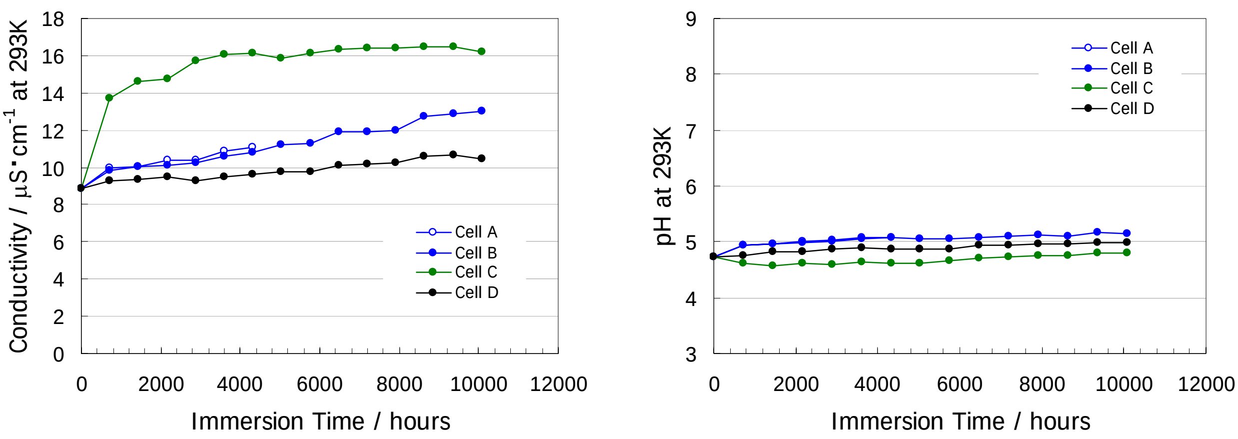

Figure 1. Conductivity and pH of the Bath

Visual Inspections

All coupons were subjected to visual inspections. The results of the visual inspections are shown in Table 2 and macro photographs of the coupon #3 and #4 (non-anodized) are shown in Figures 2 and 3. Macro photographs were taken before and after testing. All coupons had no blisters, swelling or other abnormalities that caused loss of boron carbide. For the skin, there was a small defect (see the red arrow in Figure 2). For the core, all coupons had no defect.

Table 2. Result of the Visual Inspections

Coupon #	Surface Treatment	Immersion Period	Result of the Visual Inspections			
			Blister	Swelling	Other Abnormalities	
					Skin	Core
1	non-Anodized	4,320 h	None	None	None	None
2	non-Anodized	4,320 h	None	None	None	None
3	non-Anodized	10,080 h	None	None	None	None
4	non-Anodized	10,080 h	None	None	One defect	None
5	Anodized	10,080 h	None	None	None	None
6	Anodized	10,080 h	None	None	None	None

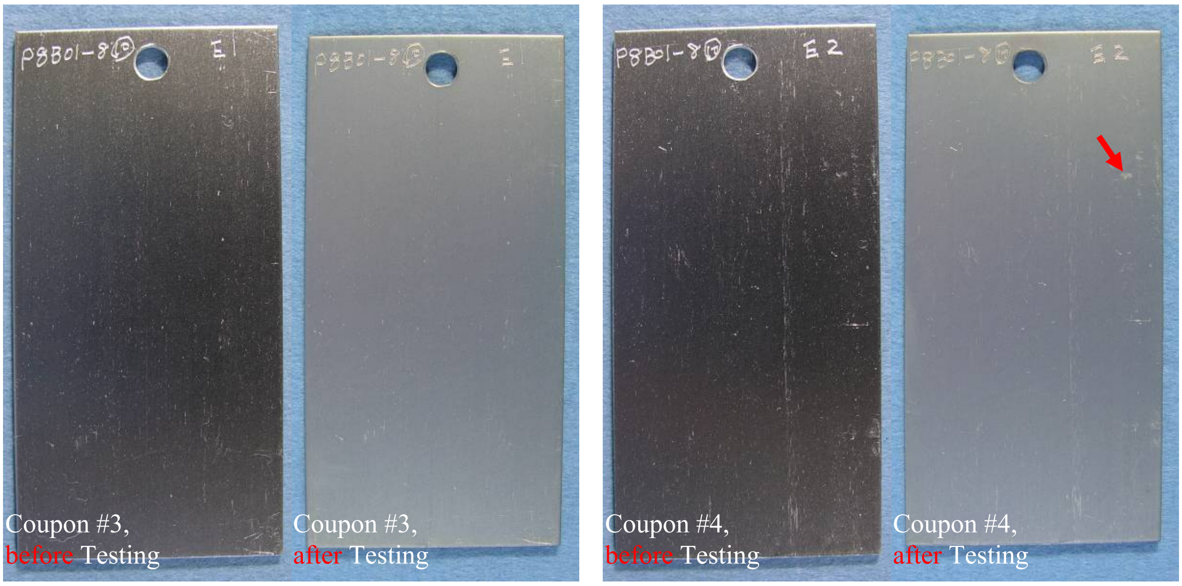

Figure 2. Macro Photographs of the Coupons before/after Immersion Testing (Top View)

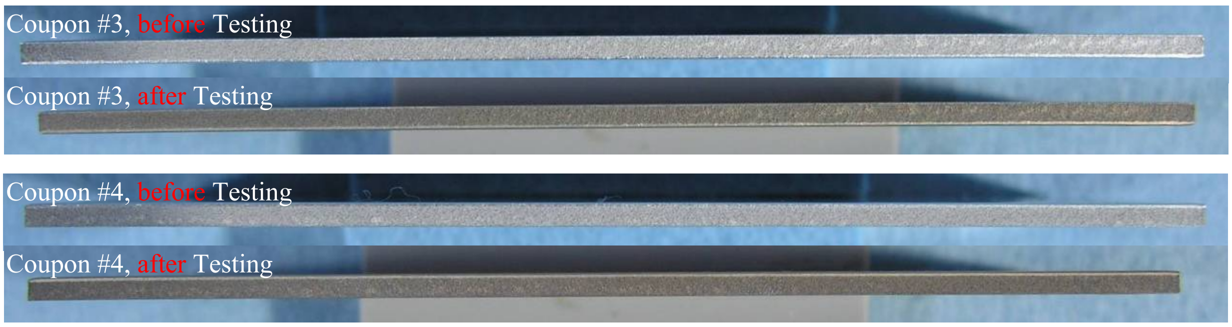

Figure 3. Macro Photographs of the Coupons before/after Immersion Testing (Side View)

Surface Defect of the Skin

Figure 4 shows the comparison of the surface defect of coupon #4 before and after testing. At the same location of the coupon before testing, an indication similar to this surface defect existed. Moreover, from this surface defect, carbon, calcium and chlorine were detected. From these results, it is thought that an organic contaminant was deposited on the surface of the coupon #4 before testing.

At the observation of the cross section, there was a dent about 15 μm deep under this defect. It is difficult to clarify whether the dent existed before testing or formed during testing. If the latter, the necessity to avoid contamination becomes obvious, even though the product's performance does not seem to be affected by this type of defect.

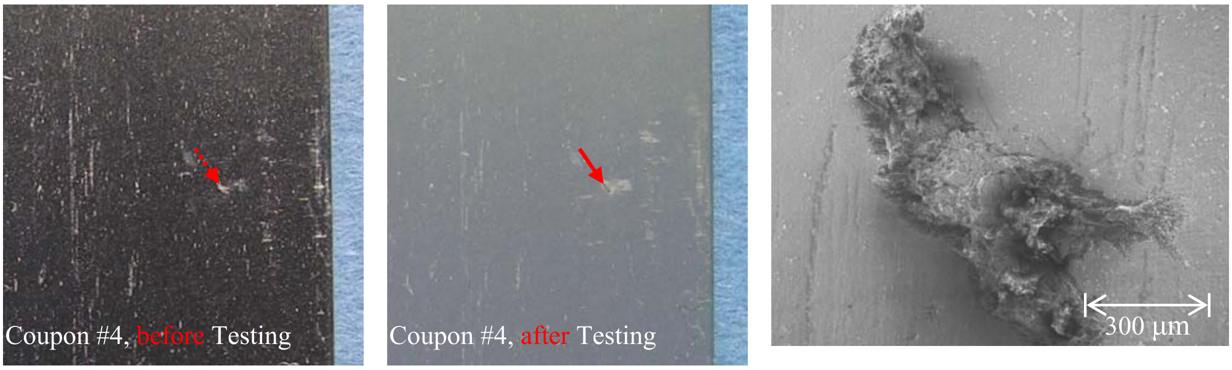

Figure 4. Macro Photographs and SEM Image of the Surface defect on the Coupon #4

Non-Anodized Coupons

Figure 5 shows the results of the surface observation of the non-anodized coupon. Due to immersion, scale-like aluminum hydrate formed on the surface of both skin and core.

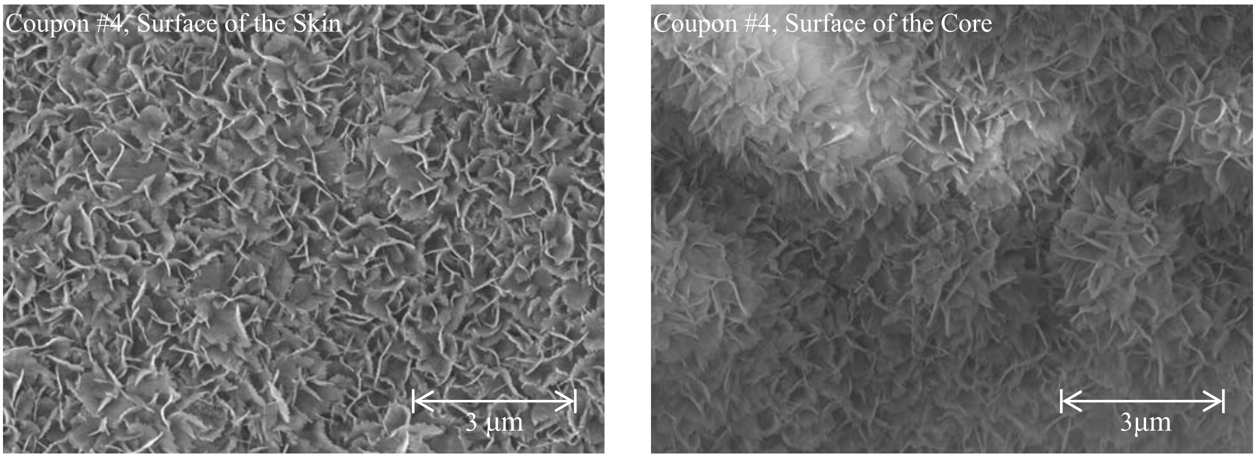

Figure 5. SEM Image for the Surface of the Skin and Core after Immersion Testing

The cross section image of the aluminum hydrate layer is shown in Figure 6. Thickness of the aluminum hydrate layer is about 2 μm, and there is no difference in that formed on skin and core.

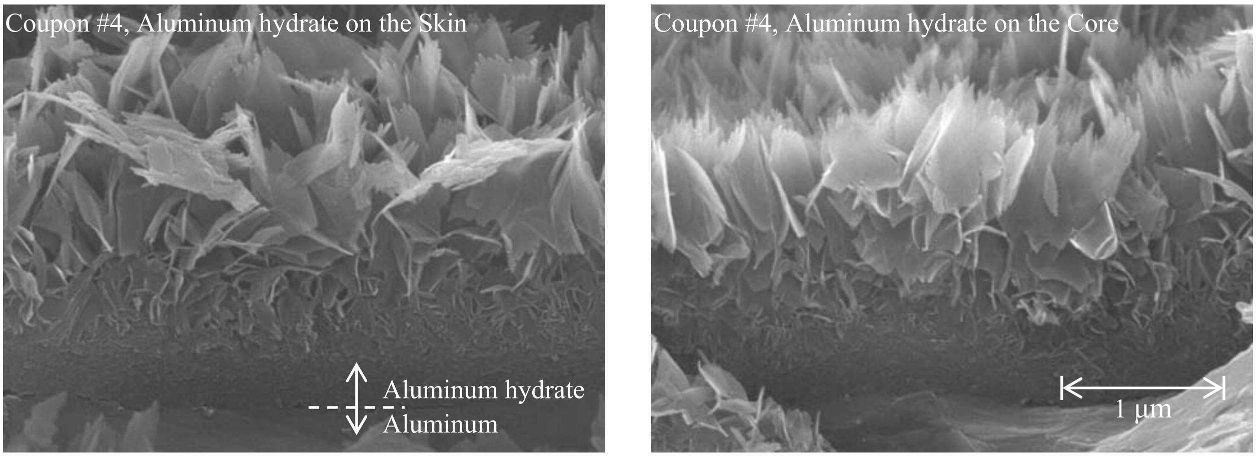

Figure 6. SEM Image for the Aluminum Hydrate on the Skin and Core

Figure 7 shows the results of the cross section observation near the surface of the core. A thick aluminum hydrate layer was formed around exposed B_4C particles. It seems that close to B_4C particles the hydration reaction of aluminum is accelerated [3]. Because clad product has a skin and the exposed B_4C particles are only on the cutting plane, the hydration reaction of the MAXUS® is less important than that of non-clad Al/B_4C products.

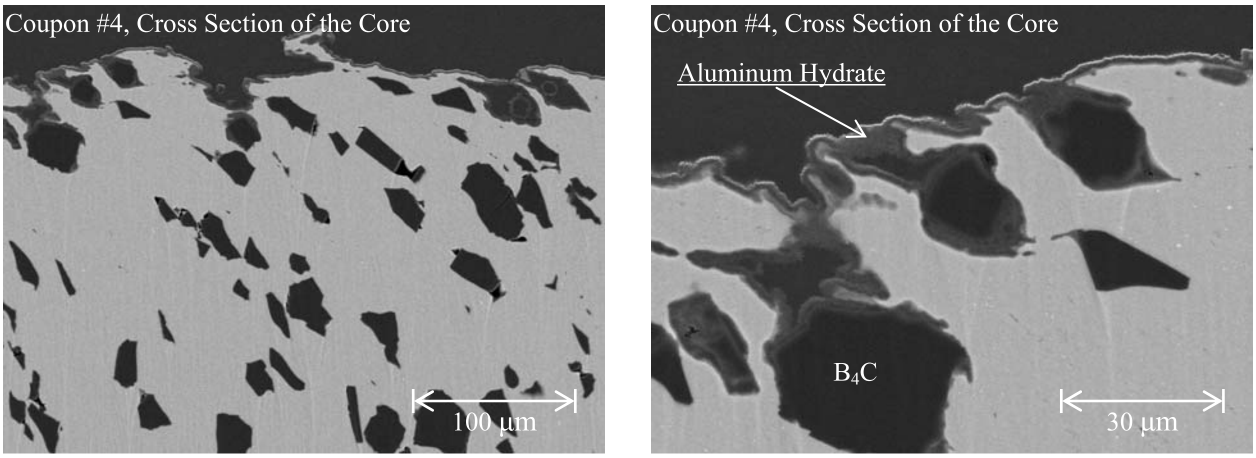

Figure 7. Electron Backscattered Image for the Aluminum Hydrate on the Core

The dry weight change before and after testing is shown in Figure 8, as well as the corrosion weight loss with removal of the aluminum hydrate in accordance with ASTM G1-03 [2]. Because there are no differences between 4,320 hours and 10,080 hours in Figure 8, it can be considered that after 4,320 hours the hydration reaction has stopped and the corrosion rate of the MAXUS® became almost zero.

The corrosion weight loss is about 0.09 mg/cm^2 and it corresponds to the dissolution of 0.6 µm in thickness as aluminum metal. The value 0.6 µm is the total loss for 10,080 hours testing, not the corrosion rate, but it is expected that the corrosion rate of the MAXUS® is considerably smaller than that of the previous study, that is a corrosion rate of 0.28 mil/year (i.e. 7 µm/year) [4]. Additionally, this value 0.6 µm is considerably smaller than the thickness of skins (190 µm a skin). The corrosion mainly affects the clad layer that is free of boron carbide. This will thus have no consequence on the neutron absorption properties of the MAXUS®. Therefore it is not considered to be significant for practical use. The corrosion rate is expected to be less than that of experimental coupons for practical use, because the ratio of cutting plane area to total surface area decreases by an increase of the plate size.

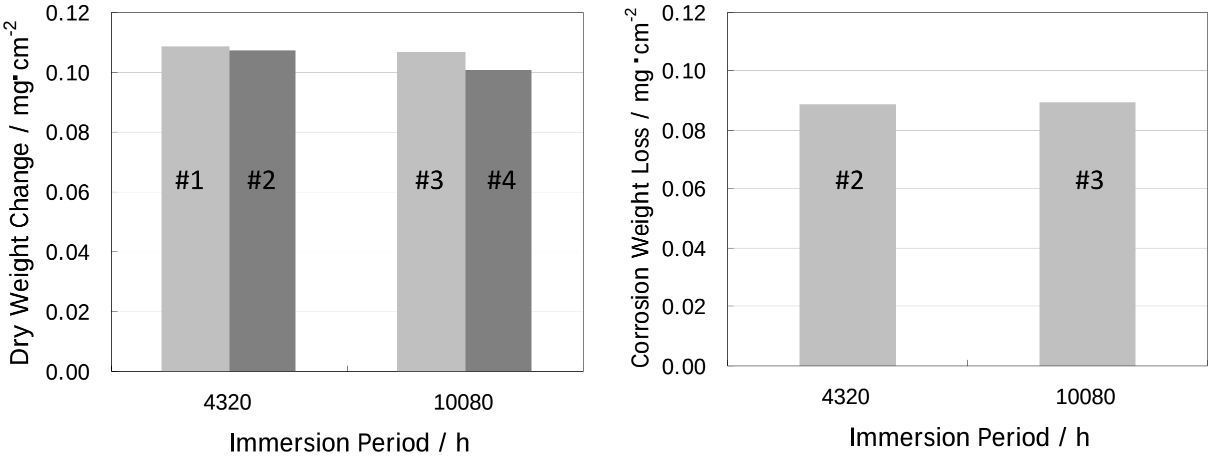

Figure 8. Dry Weight Change and Corrosion Weight Loss of non-Anodized Coupons

Anodized Coupons

Figure 9 shows the results of the observation of aluminum hydrate on the anodized coupon. There is no difference in the anodized coupon and the non-anodized coupon for the formation of aluminum hydrate. After 10,080 hours testing, the anodic film remains on the core, but there is no effect of decreasing hydration reaction.

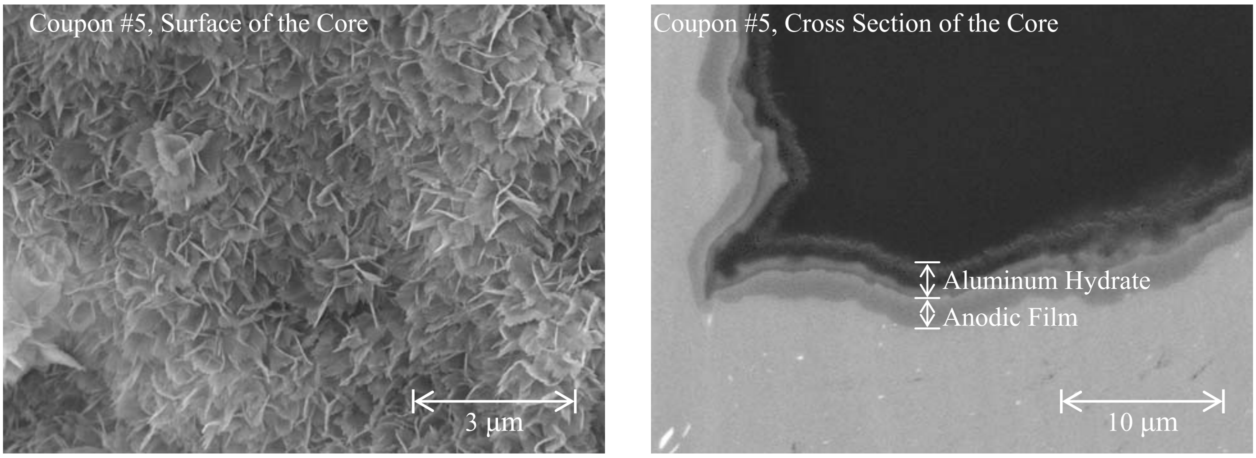

Figure 9. SEM Image and Electron Backscattered Image of the Anodized Coupon

The dry weight change before and after testing of anodized coupons is shown Figure 10. There is no difference in dry weight change before and after corrosion exposure for both anodized and non-anodized coupons. Therefore, using MAXUS® Al/B_4C MMC plate for wet storage racks does not require anodizing.

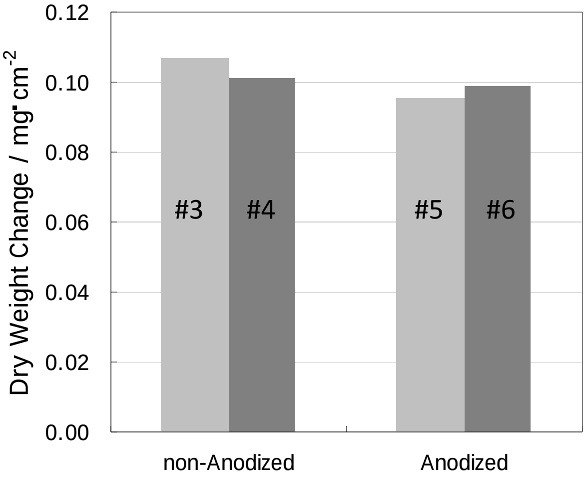

Figure 10. Comparison of Dry Weight Change in non-Anodized and Anodized Coupons

CONCLUSIONS

Accelerated corrosion testing has been performed with the MAXUS® Al/B_4C MMC plate in a simulated PWR spent fuel pool solution for 10,080 hours. All coupons had no blisters, swelling or other abnormalities that cause loss of boron carbide. For the core, all coupons had no defect. For the skin, one coupon had a surface defect. For this defect, it is thought that an organic contaminant was deposited on the surface before testing. Therefore, the necessity to avoid contamination becomes obvious, even though the product's performance does not seem to be affected by this defect.

Due to immersion, aluminum hydrate layer of about 2 μm in thickness formed on the surface of both skin and core. A thick aluminum hydrate layer was formed around B_4C particles. It seems that close to B_4C particles the hydration reaction of aluminum is accelerated. Because clad product has skin and the exposed B_4C particles exist only on the cutting plane, there is a possibility that the hydration reaction of MAXUS® is less important than that of non-clad Al/B_4C products.

The corrosion weight loss with removal of the aluminum hydrate is about 0.09 mg/cm^2, and it is not considered to be significant for practical use. Because there is no difference between 4,320 hours and 10,080 hours in this value, it can be considered that the hydration reaction with solution has stopped after 4,320 hours. For practical use, the corrosion rate is expected to be less than that of experimental coupons, because the ratio of cutting plane area to total surface area decreases by an increase of the plate size.

Since there is no difference in dry weight change before and after testing for both anodized and non-anodized coupons, using the MAXUS® Al/B_4C MMC plate for wet storage racks does not require anodizing.

REFERENCES

1. ASTM G31-72 (2004), *Standard Practice for Laboratory Immersion Corrosion Testing of Metals*
2. ASTM G1-03, *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*
3. Hongbo Ding and L. H. Hihara, Meet. Abstr. - Electrochem. Soc., vol. 802 (2008), 1668.
4. *Handbook on Neutron Absorber Materials for Spent Nuclear Fuel Applications: 2005 Edition.* EPRI, Palo Alto, CA: 2005. 1011818.