HYDROTHERMAL CORROSION OF SiC MATERIALS FOR ACCIDENT TOLERANT FUEL CLADDING WITH AND WITHOUT MITIGATION COATINGS

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Abstract

As a candidate material for accident-tolerant fuel cladding for light water reactors (LWR), SiC_f- SiC composite materials possess many attractive properties. However, prior work has shown that SiC is susceptible to aqueous dissolution in LWR coolant environments. To address this issue, candidate coatings have been developed to inhibit dissolution. For this study, CVD SiC samples were prepared with Cr, CrN, TiN, ZrN, NiCr, and Ni coatings. Uncoated SiC and SiC_f-SiC samples were also prepared. The samples were exposed for 400h in 288°C water with 2 wppm DO in a constantly-refreshing autoclave to simulate BWR-NWC. Cr and Ni coated samples lost less mass than the uncoated SiC sample, indicating an improvement in performance. The CrN coating resisted oxidation, but some of the coating was lost due to poor adhesion. The TiN coated sample gained significant mass due to oxidation of the coating. ZrN and NiCr coatings showed significant corrosion attack. SiC_f-SiC ceramic matrix composite materials dissolved much faster than the CVD SiC sample, demonstrating the need for mitigation coatings if CMCs are to be used in LWRs. This work demonstrates the promise of Cr, Ni and CrN coatings for corrosion mitigation in LWRs, and shows that NiCr and ZrN are not promising coating materials.

Introduction

The development of accident tolerant fuel cladding has been a subject of great interest since the Fukushima incident in 2011. Among the cladding materials being considered to replace Zircaloy tubing, silicon carbide (SiC) has emerged as a leading candidate material[1][2]. To overcome the brittleness of the material, ceramic matrix composite (CMC) materials have been developed in which silicon carbide is deposited onto a woven layer of silicon carbide fibers (SiC_f-SiC). Despite possessing favorable mechanical properties, high-temperature corrosion resistance[3][4], and excellent neutronics[5], SiC_f-SiC has been found to dissolve during light water reactor (LWR) normal operating conditions[6].

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To improve material compatibility, corrosion resistant coatings are being considered as a method for mitigating hydrothermal corrosion of CMC SiC during LWR normal operating conditions. Several studies have already examined corrosion mitigation coatings on Zircaloy[7]–[9]. Cr, CrN, and TiN were found to have favorable compatibility in LWR water when compared to uncoated Zircaloy.

The objective of this work is to test several candidate coatings for use on SiC cladding. Cr, CrN, and TiN coatings, which performed well as coatings on Zircaloy, were chosen for this work. Additionally, samples with Ni and NiCr coatings were tested for comparison. Additionally, ZrN was chosen as a coating to study the effect of oxidation on the adherence of the coating. The results of experiments in which coated SiC specimens are exposed to 288°C water with 2 wppm dissolved oxygen (DO) to simulate boiling water reactor normal water chemistry (BWR-NWC) are reported, to show the effectiveness of the candidate coatings. BWR-NWC was chosen as an initial test due to its aggressiveness when compared to hydrogen water chemistry (HWC). Future work will present more in-depth characterization of the samples shown in this work, along with the results of the same materials exposed to BWR-HWC and pressurized water reactor (PWR) primary water.

Experiment

Samples Prepared

For this work, coated and uncoated samples were exposed to BWR-NWC conditions (288°C, 3 wppm DO) for up to 400h. Coated coupons were prepared by applying candidate coatings to high purity, stoichiometric CVD SiC from Rohm and Haas (now Dow Chemical Company, PA). Coatings were applied by two methods. The first method was cathodic arc physical vapor deposition (PVD), in which the coating was deposited by an industrial vendor which used cathodic arc evaporation of metallic targets. The second was an electrochemical method in which a thin electroless Ni coating was applied to SiC substrates. In the case of the NiCr sample, the Ni coating was only a very thin compatibility layer, on which a conventional electroplated coating of Ni-3%Cr was applied. CVD SiC was chosen as a substrate for these preliminary tests due to the difficulty of obtaining SiC_f-SiC. It is expected that in later works, SiC_f-SiC will be used as a substrate for the coating candidates which perform best. One uncoated CVD SiC sample was also exposed for comparison. The coupons measured 25 x 6 x 1 mm with a 2 mm hole, from which the coupons were hung.

Also tested were two SiC_f-SiC matrix-composite coupons. One was a previous generation of composite using Hi-Nicalon Type-S 0.5K SiC fiber (CMC-N). The other was a contemporary composite using Tyranno SA-3 fiber (CMC-T). Both composites used a proprietary CVI/D SiC from Hypertherm (now Rolls-Royce, Ltd) for both matrix and overcoat. The major difference between the two composites was the lower density of the older generation of composites.

Table 1 shows the processing, process temperature, deposit thickness, compatibility coat and top coats by phase composition in the coatings. The phase composition of the specimens was characterized by X-ray diffraction (XRD). The sample was rotated at 10 rpm with a 2θ scan range from 10-130° under Cu Kα radiation using a Bruker D2 Phaser X-ray diffractometer (30 kV, 30 mA) equipped with a LynxEye detector. The data was analyzed by PANalytical HighScorePlus for phase identification using Powder Diffraction File (PDF) database and profile fitting conducted by Rietveld analysis. Instrumental broadening was calculated by a NIST 660 LaB6 and the samples were spiked with a NIST 640d Si standard.

Table 1. Details of the samples used for this work, including coated samples of SiC substrates, uncoated SiC_f-SiC samples, and solid samples for purposes of comparison

Sample ID	Substrate	Coating	Process	Coating Thickness (μm)	Phases
SiC	SiC	none	CVD	-	99.9% SiC
CMC-N	SiC_f	SiC	CVI/D	-	>99% SiC
CMC-T	SiC_f	SiC	CVI/D	-	99.9% SiC
Solid Cr	Cr	none	Cast	-	Not Measured
Solid TiN	TiN	none	Hot Pressed	-	TiN
Ni-SiC	CVD SiC	Ni	Electrochemical	30	Ni
NiCr-SiC	CVD SiC	NiCr	Electrochemical	40	Ni, Ni-3%Cr
Cr-SiC	CVD SiC	Cr	PVD	20	Cr
CrN-SiC	CVD SiC	CrN	PVD	30	$CrN_{(1-x)}$/Cr
TiN-SiC	CVD SiC	TiN	PVD	5	$TiN_{(1-x)}$ /Ti
ZrN-SiC	CVD SiC	ZrN	PVD	5	$ZrN_{(1-x)}$ /Zr

Experimental Procedure

Exposures were conducted using a controlled chemistry water loop at the Hydrothermal Corrosion Laboratory (HCL) at Oak Ridge National Laboratory. A schematic of the water loop is shown in Figure 1. Samples were hung from zirconia rods in the 3.8 L

Hastelloy 276 autoclave. A gas blend of 95% argon and 5% oxygen was bubbled through the main column to maintain a dissolved oxygen (DO) concentration of ~2 wppm. Water from the column was fed to a Pulsafeeder high-pressure pump which maintained a pressure of 1900 psi. Water was heated by a pre-heater and a heating band over ~3-4 hours to 288°C and maintained for 200h before cooling to room temperature. Water flowing from the autoclave was chilled and depressurized before flowing into a clean-up column where it was collected, and then run through a series of DI filters and a UV light before recirculating into the supply column.

Samples we exposed for 2 cycles of 200h. They were characterized using light microscopy and scanning electron microscopy (SEM), and were weighed to determine mass change.

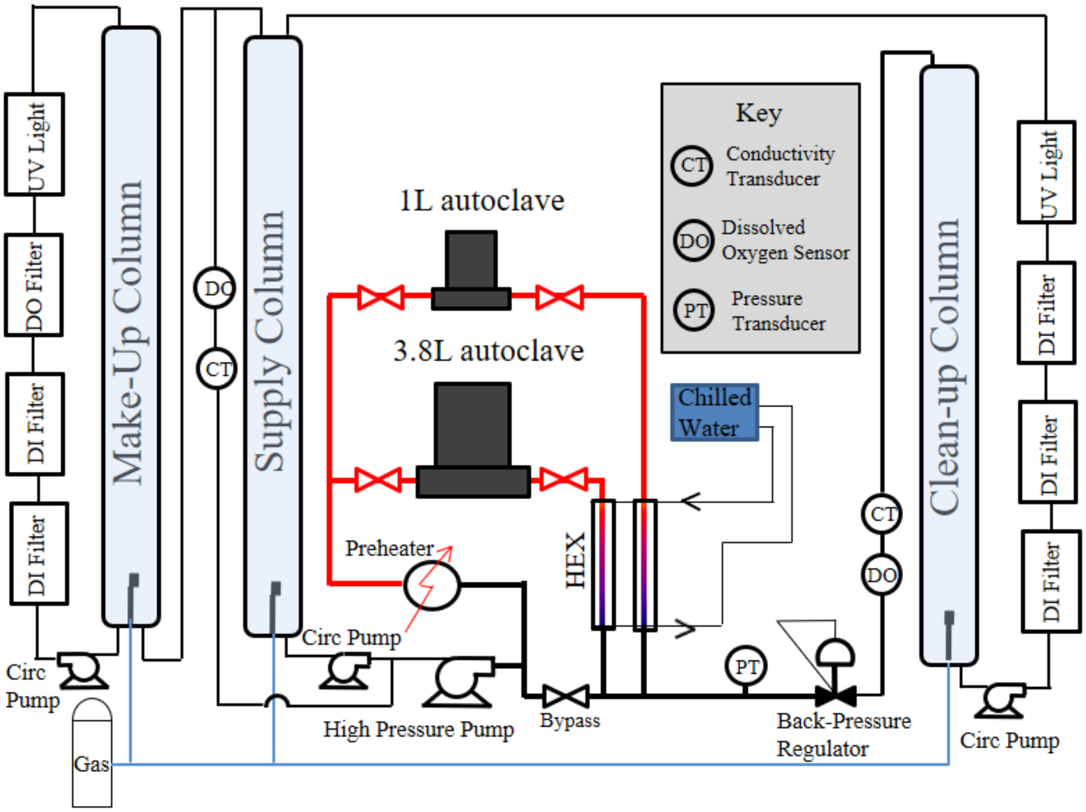

Figure 1. Schematic drawing of the controlled chemistry water loop at the hydrothermal corrosion laboratory at ORNL.

Results

To measure mass change, samples were weighed before exposure, after 200h, and after 400h, and the results are shown in Figure 2.

Both the solid TiN coupon and the TiN-coated coupon gained mass during the exposures, suggesting the growth of an adherent oxide film.

The SiC_f-SiC coupons both lost significant mass at a linear rate, while the uncoated CVD SiC sample lost a small amount of mass. Terrani et al. [6] reported a similar mass loss for a CVD-SiC sample exposed to NWC, but reported a mass *gain* for a sample of Tyranno SiC_f-SiC during the first month of exposure, which disagrees with the mass loss observed after 400h in this work. The reason for this discrepancy is not clear

The solid Cr coupon and the Cr-coated coupon both lost mass at a relatively slow, and relatively linear rate. The solid Cr coupon was cut from a drop-cast with large visible pores, and it is hypothesized that this porosity accounts for the higher rate of mass loss seen in the solid Cr coupon (0.23 mg/cm^2 after 400h) compared to the mass loss of the Cr coated coupon (0.026 mg/cm^2 after 400h). The CrN coated sample lost mass at a higher rate during the first 200h exposure, and the rate of mass loss slowed during the second exposure. The partial spallation visible on the CrN coated coupon (Figure 3) is the likely reason for the higher rate of initial mass loss, and the slower rate of mass loss after 200h suggests that CrN may still be a viable mitigation coating. Future characterization of the coating will aid in this determination. The Ni coated sample gained a slight amount of weight during exposure, likely due to oxidation of the Ni coating to form NiO, which will be determined with future work. NiCr and ZrN coated samples lost mass rapidly during the first 200h exposure, but the rate of mass loss slowed or stopped during the second exposure.

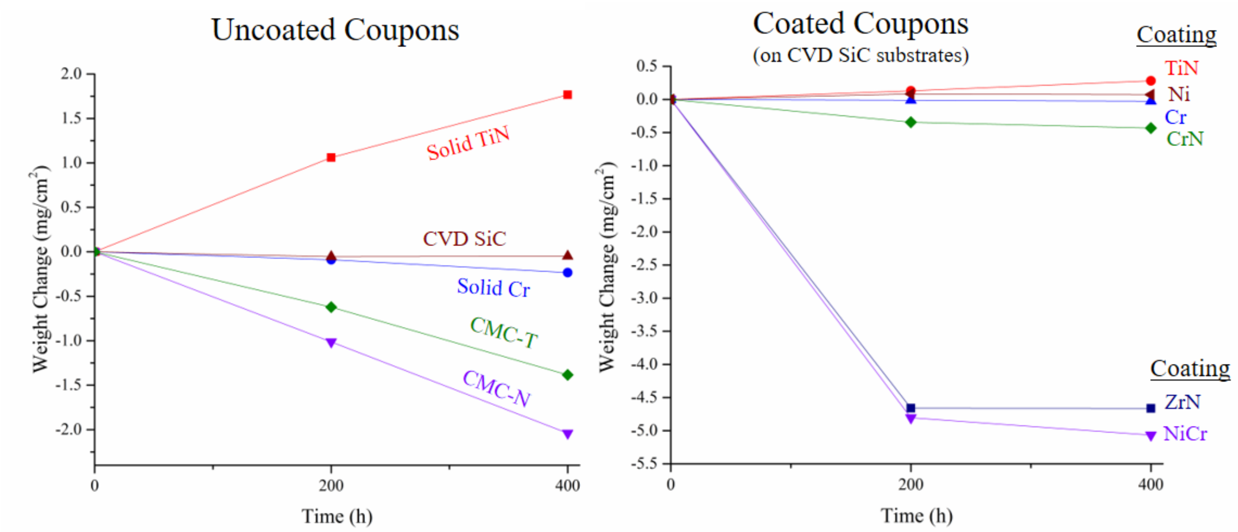

Figure 2. Mass change of (a) coated and (b) uncoated coupons. Values are graphed as the change in mass relative to the coupon mass before exposure.

Light micrographs of the coated coupons before exposure, after 200h of exposure, and after 400h of exposure are shown in Figure 3. Significant spallation of the CrN and NiCr coatings is visible in the images, and it appears the majority was lost during the first 200h exposure. Aside from the spalled areas, the CrN coating shows little sign of corrosive attack where the coating remained adherent. The Cr coated coupon shows little sign of corrosion or spallation. The TiN and ZrN coupons show significant signs of corrosive attack. This is most easily seen by observing the difference in surface color and finish between the center regions of the coupons and the edges. Further characterization is planned for the future to better understand the nature of the corrosive attack.

The ZrN coupon's rapid weight loss appears to be the result of this attack, as no spallation is visible on the sample. The rapid weight loss of the NiCr coupon during the initial 200h exposure, however, was likely due to large area from which the coating spalled, shown in Figure 3. The sample continued to lose mass during the second exposure, suggesting the coating is not a good candidate, even if it were to adhere to the substrate. The ZrN coupon did not lose mass during the second exposure, after a rapid mass loss during the first exposure. The images in Figure 3 do not show any spallation, so it is likely that the initial weight loss is due to corrosive attack, and the lack of weight change during the second exposure is possibly due to the growth of an adherent film concurrent with corrosive dissolution. Due to the rapid corrosive attack, ZrN is not a good candidate as a mitigation coating.

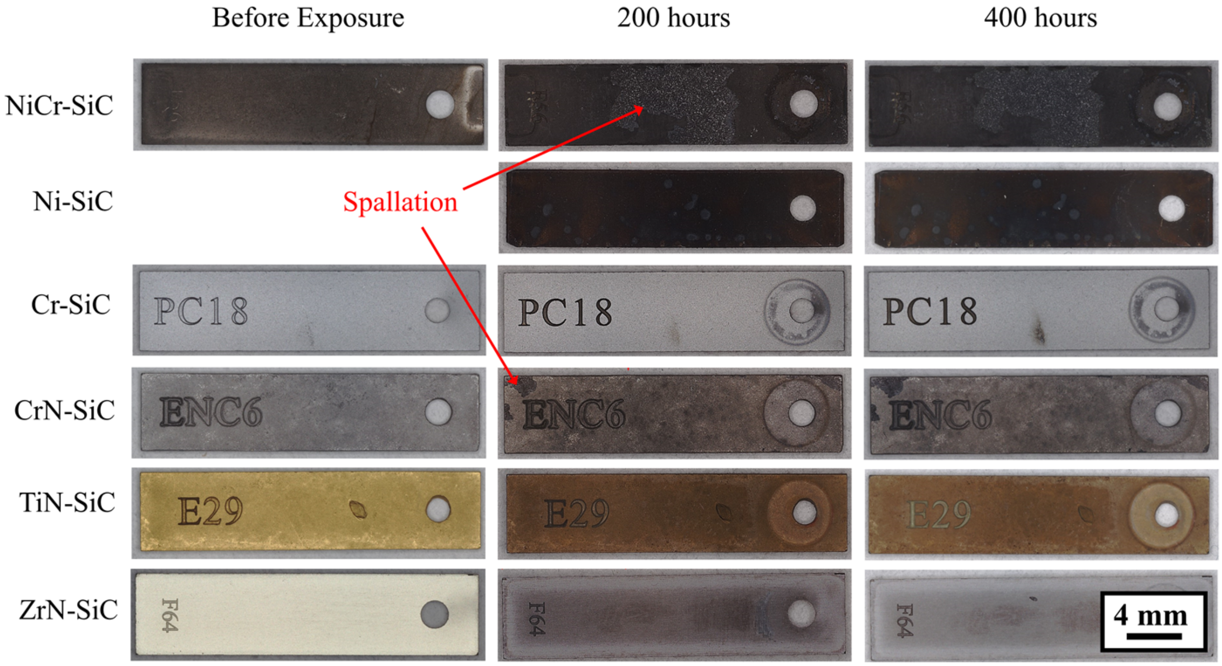

Figure 3. Light micrographs of coated coupons imaged before exposure, after 200h, and after 400h of exposure. Six different coupons are shown, each with a different coating applied to a SiC substrate. The Ni coated sample was not imaged prior to exposure.

Light micrographs of the uncoated SiC, SiC_f-SiC, and solid coupons before exposure, after 200h of exposure, and after 400h of exposure are shown in Figure 4. Some signs of attack are visible on the SiC_f-SiC samples, but very little change is visible on the uncoated SiC sample. The solid Cr and TiN samples show some signs of a surface oxide. The irregular shape of the TiN coupon is due to difficulty machining the material.

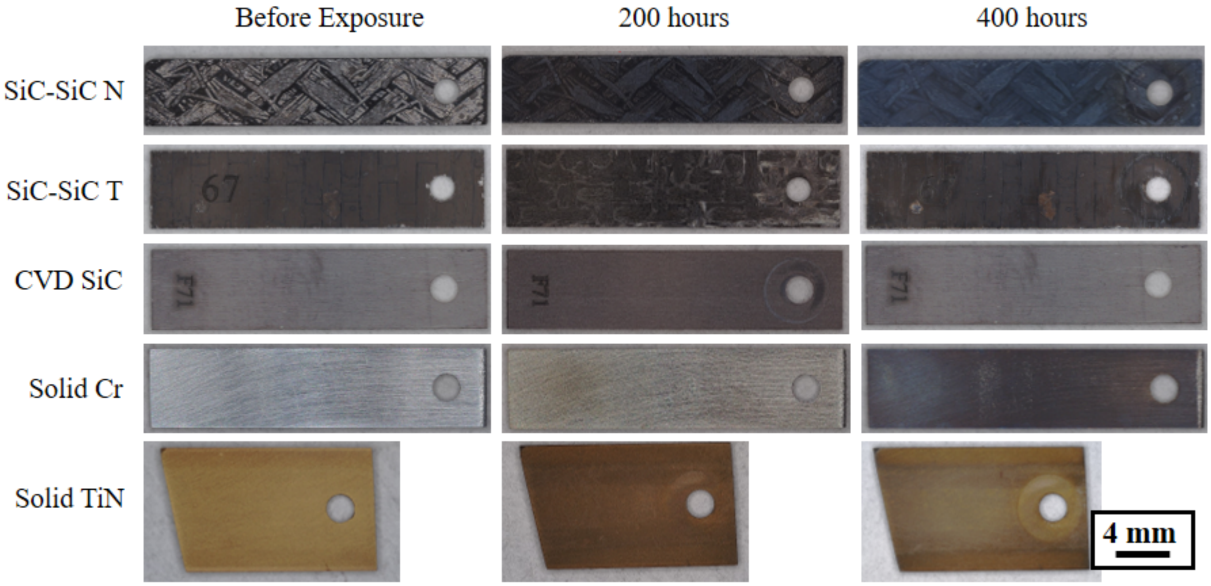

Figure 4. Light micrographs of uncoated SiC, SiC_f-SiC, and solid coupons before exposure, after 200h, and after 400h of exposure.

SEM-EDS images of the Ni-3Cr coated sample are shown in Figure 5. The Si signal indicates areas where the coating spalled, and the SiC substrate is visible. The coating has oxidized, as shown by the oxygen signal on the areas where the NiCr coating remains.

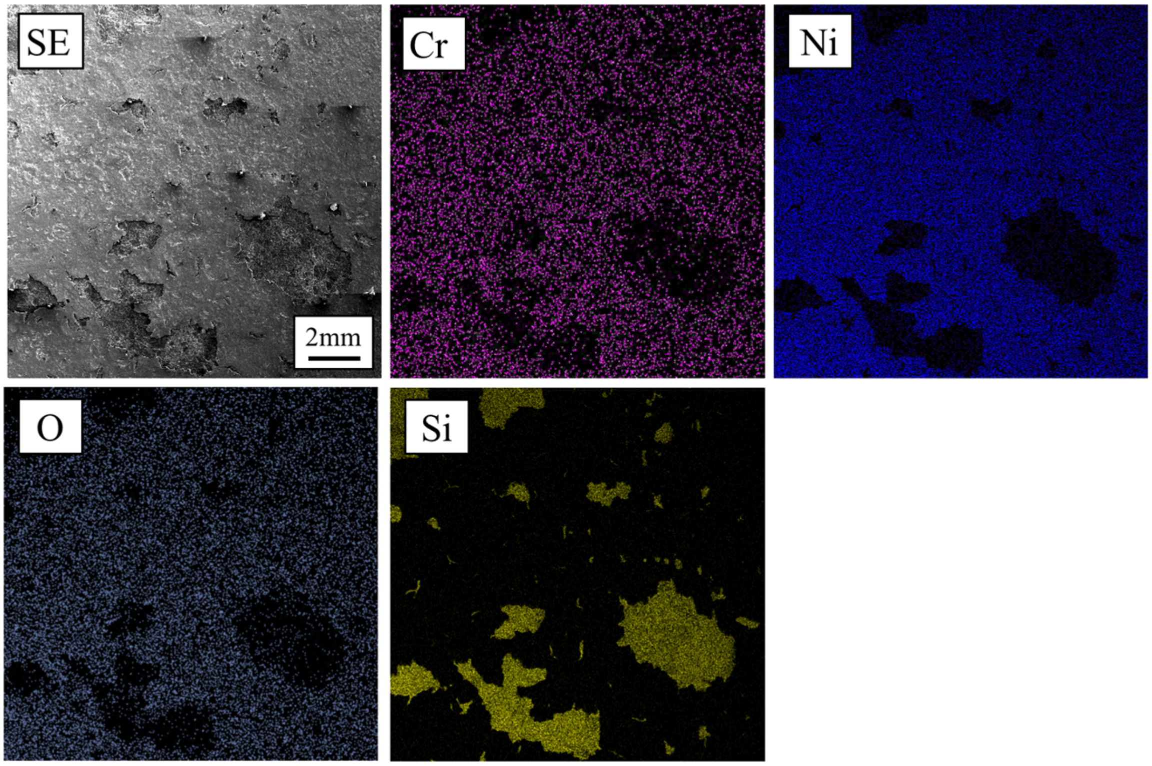

Figure 5. SEM-EDS images of the NiCr coated sample

SEM-EDS images of the CrN coated sample are shown in Figure 6. As with the NiCr sample, the area on which spallation occurred is visible by the strong Si signal. The much weaker oxygen signal indicates that the CrN coating did not oxidize as much as the NiCr coating.

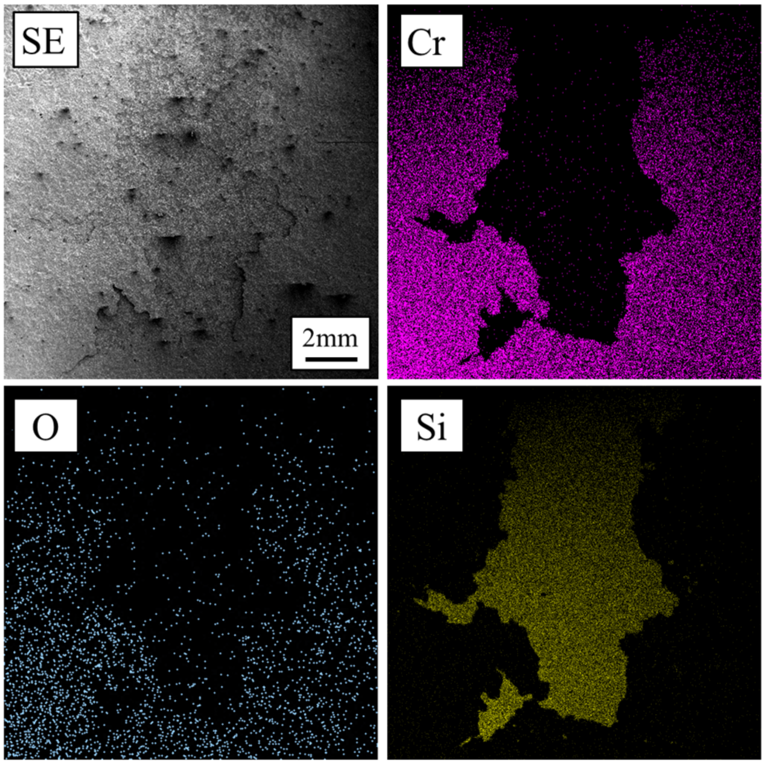

Figure 6. SEM-EDS images of the CrN coated sample

Conclusions

After 400h of autoclave exposure, the Ni and Cr coatings exhibited the least amount of mass change. The CrN coupon lost more mass than the Cr coupon, but examination of the coupons showed little oxidation, so it appears that the coating may perform acceptably, and the mass loss can be attributed to poor adhesion of the coating to the substrate. The TiN coated coupon gained significant mass, consistent with the even greater mass gain shown by the solid TiN coupon, both attributable to oxidation of the coating material. The ZrN and NiCr coated coupons lost the most mass, and showed significant signs of corrosive attack. The preliminary results shown in this work will be supplemented with additional characterization in the future to better determine the nature of corrosive attack and coating adherence. Based on the results shown in the present work, Ni, Cr, and CrN show the most promise for future study as a coating material on SiC_f-SiC ceramic matrix composite cladding.

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