Corrosion Behaviour of Porous Chromium Carbide/Oxide Based Ceramics in Supercritical Water

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Abstract

Porous chromium carbide with a high density of open pores was fabricated by a reactive sintering method. Chromium oxide ceramics were obtained by re-oxidizing the porous chromium carbides formed. Some samples were added with yttria at 5 wt. %, prior to reactive sintering to form porous structures. Corrosion tests in SCW were performed at temperatures ranging from 375°C to 625°C with a fixed pressure at around 25~30 MPa. The results show that chromium carbide is stable in SCW environments at temperatures up to 425°C, above which disintegration of carbides through oxidation occurs. Porous chromium oxide samples show better corrosion resistance than porous chromium carbide, but disintegrate in SCW at around 625°C. Among all the samples tested, chromium oxide ceramics with added yttria exhibited much better corrosion resistance compared with the pure chromium carbide/oxides. No evidence of weight change or disintegration of porous chromium oxides with 5 wt % added yttria was observed after exposure at 625°C in SCW for 600 hours.

Keywords: SCWR, Chromium Carbide, Chromium Oxide, Corrosion, Yttria

1. Introduction

The Supercritical Water-cooled Reactor (SCWR) is one of the most promising advanced reactor concepts proposed for Gen-IV nuclear reactors [1]. Using SCW as a coolant offers many advantages, such as higher thermal efficiency (i.e., 45-48% versus about 30-35% efficiency for current LWR), reduced size of reactor components and simplification of the reactor design, as the steam generators, steam dryers, steam separators, are eliminated [2]. Besides the benefits, using SCW as the coolant also leads to some materials challenges, since SCW has never been used in nuclear power application. SCW can be very aggressive especially when some oxidative species present. Water may also be involved in corrosion reaction under the high temperature and pressure conditions. Although extensive research has been conducted on the materials used in SCW environments for existing applications (e.g., fossil fuel combustion plants, supercritical water oxidation reactors), the investigation of the materials used in SCWR is necessary for the different SCW conditions and irradiation environment.

Ceramic materials usually exhibit better chemical stability and higher corrosion resistance as compared to metallic materials, and can potentially be used as structural or insulator materials in SCW environments. The stability of various ceramics in different SCW environments has been investigated by some scientists [3-5]. In the work conducted by Boukis et al. [3], it was observed that HIP-BN, B_4C, TiB_2, Y_2O_3 and Y-TZP disintegrated after being exposed to SCW containing 0.44 mol kg^{-1} oxygen and 0.05 mol kg^{-1} hydrochloric acid at a temperature of 465°C and a pressure of 25 MPa. SiC- and Si_3N_4- based materials showed a large weight loss of up to 90%. Homogeneous surface attack and grain boundary diffusion were observed for the ceramic samples tested. Monolithic Al_2O_3 showed better corrosion resistance than mixed Al_2O_3 with ZrO_2. Partially stabilized zirconia (PSZ) exhibited better corrosion resistance in SCW. Schacht et al. [4] systematically examined the corrosion resistance of alumina ceramics and zirconia toughened alumina (ZTA) ceramics in aqueous acidic solutions (HCl, H_2SO_4, H_3PO_4) under hydrothermal conditions. It was found that the dominant corrosion mechanisms for Al_2O_3 in hydrothermal conditions were intergranular attack with dissolution of Al_2O_3. Guzonas et al. [5] conducted the investigation on the performance of zirconia films exposed to SCW conditions in a static autoclave. The results show that zirconia films can improve the corrosion resistance of carbon steel and reduced the corrosion rate by a factor of 1.6-2. To our knowledge, little investigation has been conducted on the performance of chromium carbide/oxide based ceramics in SCW environments, in particular those of relevance to an SCWR. Cr_3C_2 possesses some unique properties, such as high hardness and Young's modulus, medium fracture toughness, excellent high-temperature erosion and wear resistance, low density, high-temperature and chemical stability [6-8]. Cr_3C_2 is usually thermally sprayed to protect the underlying metal surface, or used as an additive in coatings to increase their resistance to corrosion and wear. Cr_2O_3 exhibits excellent chemical stability in oxidative environments at elevated temperature. It can potentially be used as coating or insulation material in SCW environments. Chromium is also the oxide-forming element for many potential candidate alloys being considered for use in an SCWR. Therefore it is useful to investigate the performance of chromium carbide/oxide based ceramics in SCW conditions. In this report, porous chromium carbide/oxide based ceramics were tested under various SCW conditions at temperatures ranging from 375°C to 625°C with a fixed pressure of 25~30 MPa. The effect of the temperature on the stability of the ceramics was evaluated. Some oxides samples with added yttria were tested to evaluate the effect of yttria on the stability of chromium oxide ceramics in SCW.

2. Expermental

Chromium oxide powder (Alfa Aesar, USA, average particle size P_s of ~2µm, purity of 99%) and yttrium oxide powder (Alfa Aesar, USA, average particle size P_s <1µm, purity of 99%) were used as starting materials. Chromium oxide powder was uniaxially compressed in a cylindrical mold at a pressure of 80 MPa to form disk-shaped samples with a diameter of 16 mm and thickness of 2 mm. The disk shaped samples were put into a tube furnace (GSL1600X, MTI Corporation) and heated to 1000°C, 1100°C, 1200°C and 1300°C, respectively, in a reducing gas mixture (2%CH_4 + 98%H_2, Praxair Canada) at a flow rate of 140 ml/min. Some samples were also mixed with yttrium oxide powder at 5 wt. %. The mixing was done by ball milling using high purity alumina balls (13 mm in diameter) and ethanol for 10 hours. The mass ratio of ball to powder was 8:1.

Morphologies of ceramic samples were examined by JEOL (JSM-6301FXV) field emission scanning electron microscope and ZEISS (EVO –MA15) SEM. X-ray diffraction (XRD) analysis was carried out using a Rigaku Geigerflex 2173 X-ray diffraction equipment. The porous properties of the as-carburized samples were characterized using a mercury intrusion porosimeter (AutoPore IV 9510).

The ceramic coupons tested in SCW environment were cut from disk samples with a size of 10mm×4mm×2mm. The coupons were cleaned in ethanol in an ultrasonic water bath to remove debris. Then the coupons were sealed in static reactors with controlled amount of deionized water and heated in a tube furnace. The static reactor was made of a 65 mm length of Inconel 625 alloy tubing, with an outside diameter of 9.525 mm and a wall thickness of 1.651 mm. Only one coupon was put in each reactor. The neutral deionized water with an oxygen concentration of about 8 ppm was used in SCW tests. No purge procedure was performed before the reactors were sealed, therefore some air should be present.

3. Results and Discussion

3.1 Fabrication of porous ceramics

3.1.1 Porous chromium carbide ceramics

The surface morphology of the pure Cr_2O_3 sample before sintering is shown in Figure 1(a). It can be seen that the micrometer sized Cr_2O_3 particles were compacted together, and were mainly bonded by electrostatic forces across the particle interface. The porosity of the compact samples calculated from the sample dimensions and mass is about 36.9-40.7 %. Figures 1 (b) and (c) show SEM micrographs of the surface and cross-section for the sample obtained by reactive sintering in a reducing atmosphere ($2\%CH_4 + 98\%H_2$) at a sintering temperature of 1100°C for 10 hours. The sample after sintering exhibited a remarkably homogeneous porous morphology with a smooth three-dimensional network skeleton structure. The phase of this porous sample was identified as Cr_3C_2 by X-ray diffraction analysis, as shown in figure 2.

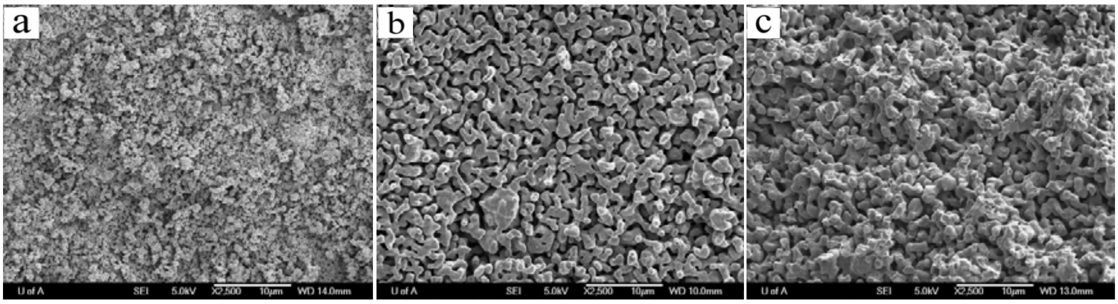

Figure 1 SEM micrographs of the 100% Cr_2O_3 green disk before sintering (a), after sintering at 1100°C in a reducing atmosphere ($2\%CH_4 + 98\%H_2$) for 10 hours: (b) surface and (c) cross-section.

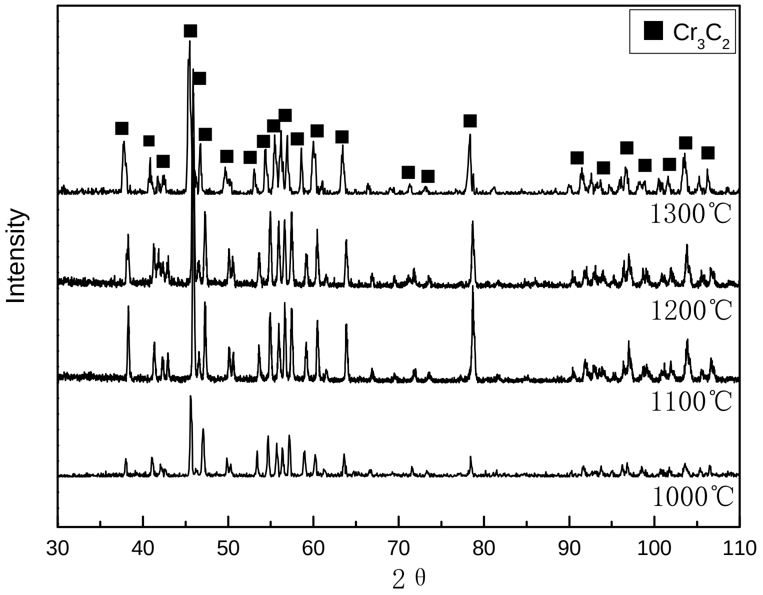

Figure 2 X-ray diffraction patterns of pure Cr_2O_3 samples after carburizing at a) 1000°C; b) 1100°C; c) 1200°C; d) 1300°C for 10 hrs.

Figure 3 shows the variations in microstructure of sintered samples with different sintering temperatures. The porous structure carbides were characterized by mercury intrusion porosimeter and the results are listed in Table 1. It can be seen that the pore size increased with the increase of sintering temperature, while the porosity decreased with temperature. The reticulated carbide sintered at 1000°C exhibited a fine porous structure with a average pore diameter of about 0.5 µm. When the sample was sintered at 1300°C, the porous structure became coarser and the pore size increased to 2~3 µm. The porosity of the porous carbide could reach about 77 % when the sample was sintered at 1000°C and 1100°C, and it decreased to about 52 % when the sintering temperature increased to 1300°C.

Table 1 Porous properties of as-carburized sample at different temperatures

Carburization Temperature(°C)	1000	1100	1200	1300
Total Pore Area (m^2/g)	1.589	0.718	0.497	0.338
Average Pore Diameter (nm)	527.6	1167.0	1601.4	2415.2
Porosity	76.01%	77.76%	66.68%	51.96%

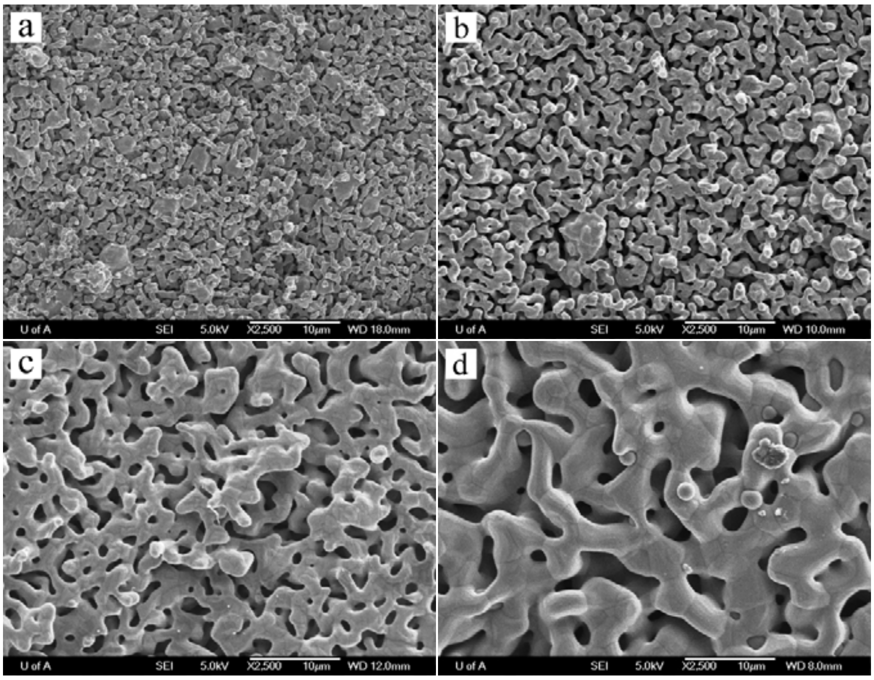

Figure 3 SEM micrographs of pure Cr_2O_3 samples after carburizing at different temperatures in a reducing atmosphere (2% CH_4 + 98% H_2) for 10 hours respectively: a)1000°C; b) 1100°C; c) 1200°C; d) 1300°C.

The mechanism of Cr_2O_3 reduction by methane-hydrogen gas has been investigated by some scientists using different methods. Read et al. concluded that the role of methane was to supply carbon, and carbon diffuses into the oxide, based on the observation that non-isothermal reduction of chromium oxide by solid carbon in a hydrogen atmosphere was similar to that by a methane-hydrogen gas mixture [9]. Anacleto et al. suggested the carburization reaction serves as a sink for adsorbed carbon, which provides a higher extent of the reduction reaction [10]. After completion of this reaction, adsorbed carbon is not consumed and forms solid carbon. All studies are in agreement that the carburization of Cr_2O_3 takes place according to the following equation.

$$3Cr_2O_3\,(s) + 13CH_4\,(g) = 2Cr_3C_2\,(s) + 9CO\,(g) + 26H_2\,(g) \qquad (1)$$

The transformation of Cr_2O_3 to Cr_3C_2 is accompanied by a reduction in volume, which is calculated to be about 38.3% (density: Cr_2O_3 5.22g/cm^3, Cr_3C_2 6.68g/cm^3). The initial porosity of the pressed sample disk is about 36.85-40.73%. After carburization at 1000°C and 1100°C, the porosity increased to 76.01% and 77.76%, which agrees well with the calculated volume shrinkage. It can be concluded that the porous structure was produced due to the volume shrinkage of the phase transformation. Surface energy reduction accompanied by the volume shrinkage leads to the formation of the smooth strut surface.

3.1.2 Preparation of porous chromium oxide ceramics

Porous chromium oxide can be obtained by oxidizing porous chromium carbide at elevated temperature in an oxidative environment. Figure 4(a) shows the morphologies of the samples that were carburized in a reducing atmosphere (2% CH_4 + 98% H_2) at 1100°C for 15 hours to form a porous structure with open pores, and then were oxidized in air at 800°C for 25 hours. Figure 4(b) shows the microstructure of the sample with added yttria at 5 wt. % after the re-oxidizing process. Compared with the strut surface of the porous Cr_3C_2, the strut of the porous oxide ceramics became coarsened after oxidation. Fine Cr_2O_3 crystals covered the surface of strut. Small clusters consisting of small particles were observed on the sample with added yttria as shown in Figure 4(b). EDS analysis indicates that the clusters were enriched in yttrium. XRD patterns of chromium oxide sample with 5 wt. % added Y_2O_3 is shown in Figure 5. Besides evident Cr_2O_3 and Y_2O_3 peaks, some weak peaks correspond to $YCrO_3$ appeared. No spallation was observed for any of the chromium oxide based ceramic samples prepared.

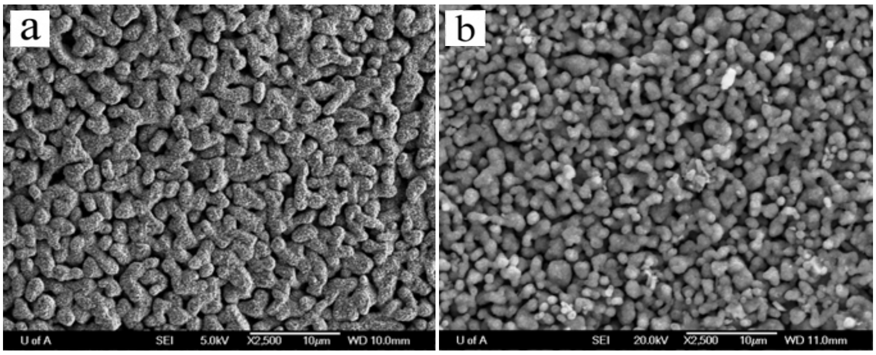

Figure 4 Morphologies of the porous Cr_2O_3 formed by oxidation of porous Cr_3C_2 at 800°C in air for 25 hours: (a) without yttria addition; (b) with added yttria at 5 wt. %.

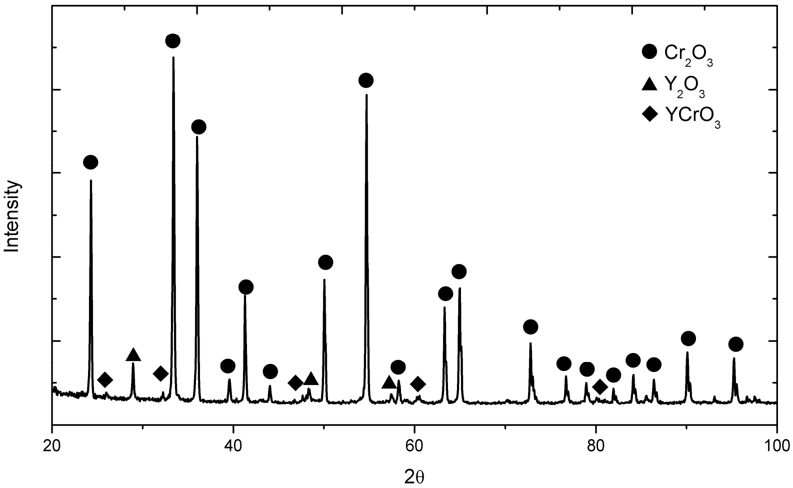

Figure 5 X-ray diffraction patterns of chromium oxide sample with 5 wt. % added Y_2O_3

3.2 Corrosion tests in various SCW conditions

3.2.1 Stability of chromium carbide in SCW environments

The SCW test results for porous chromium carbide are shown in Table 3. No disintegration of the porous chromium carbide was observed until the temperature of the SCW reached 450°C. A weight gain was observed for the coupons exposed to SCW at 375°C and 425°C. Carbide coupons tested in SCW at 450°C and 625°C disintegrated after exposure to SCW for 25 hours. SEM images of the samples after SCW test at 450°C are shown in Figure 6 (a) and (b). It can be seen that grooves appeared on the grain surface, indicative of corrosion. XRD analysis revealed that chromium carbide was partially oxidized to chromium oxide, as shown in Figure 7. The phase transformation from Cr_3C_2 to Cr_2O_3 accompanied by an increase of volume may be the reason for the occurrence of cracking and disintegration.

Table 3 Corrosion test of porous Cr_3C_2 in different SCW environments

SCW condition	Exposure time (h)	dG/G*
375°C, 25~30 MPa	25	+0.0014
425°C, 25~30 MPa	25	+0.1016
450°C, 25~30 MPa	25	disintegrated
625°C, 25~30 MPa	25	disintegrated

* dG-weight change after SCW testing; G-initial specimen weight before test.

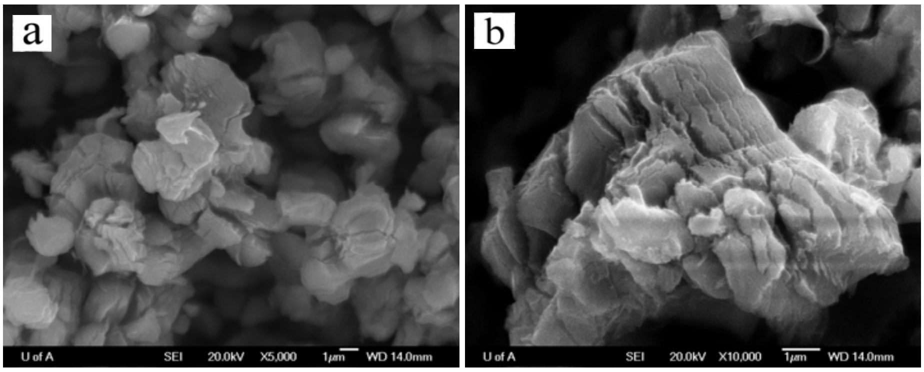

Figure 6 Morphologies of the porous Cr_3C_2 after 25 hours test in SCW at 450°C (a) low mag. (b) high mag.

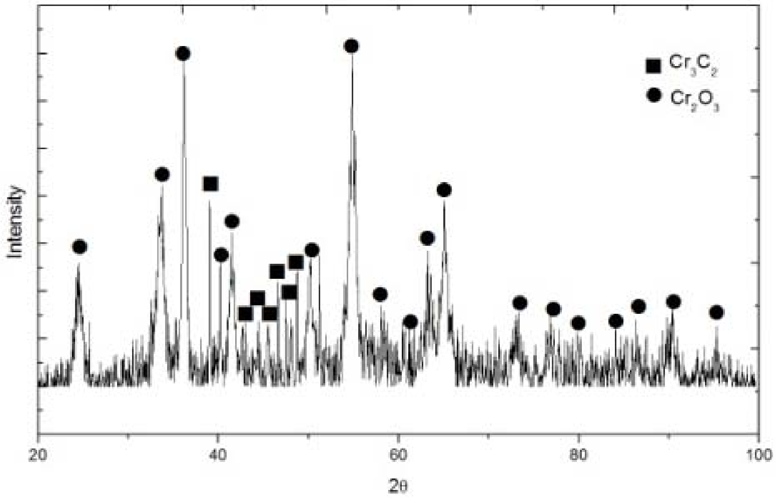

Figure 7 XRD patterns of chromium carbide samples tested in SCW at 450°C.

3.2.2 Stability of chromium oxides in SCW environments

Chromium oxide coupons were prepared by re-oxidizing the chromium carbide samples at 800°C in air for 25 hours, and then tested in SCW at temperatures of 375°C, 450°C and 625°C with a fixed pressure at around 25~30 MPa. The test results are shown in Table 4. Compared to the chromium carbides, the chromium oxide exhibited better stability in SCW environment. There was no measureable weight change for the chromium oxide sample exposed to SCW at 375°C for up to 100 hours. A very small weight loss, about 0.4%, was measured after testing at 450°C for 100 hours in SCW. However, partial disintegration occurred when the temperature of SCW increased to 625°C. Some cracks appeared on the surface of the chromium oxide sample, as shown in Figure 8 (a). High magnification SEM images (Fig. 8 (b)) reveal that those cracks apparently grew along the fine Cr_2O_3 grain boundaries. Intergranular corrosion might have occurred during the test. The Cr^{3+} ion in grain boundary region usually possesses a higher energy, and might be more easily oxidized to CrO_4^{2-} in a SCW environment. Additionally, some impurity elements may aggregate in grain boundaries, which can further weaken the stability of the grain boundary in SCW.

Table 4 Corrosion test of porous Cr_2O_3 in different SCW environments

Sample	SCW condition	Exposure time (h)	dG/G
Cr_2O_3	375°C, 25~30 MPa	100	0
Cr_2O_3	450°C, 25~30 MPa	100	-0.004
Cr_2O_3	625°C, 25~30 MPa	100	Partially disintegrated
5wt.% Y_2O_3	625°C, 25~30 MPa	600	<0.001

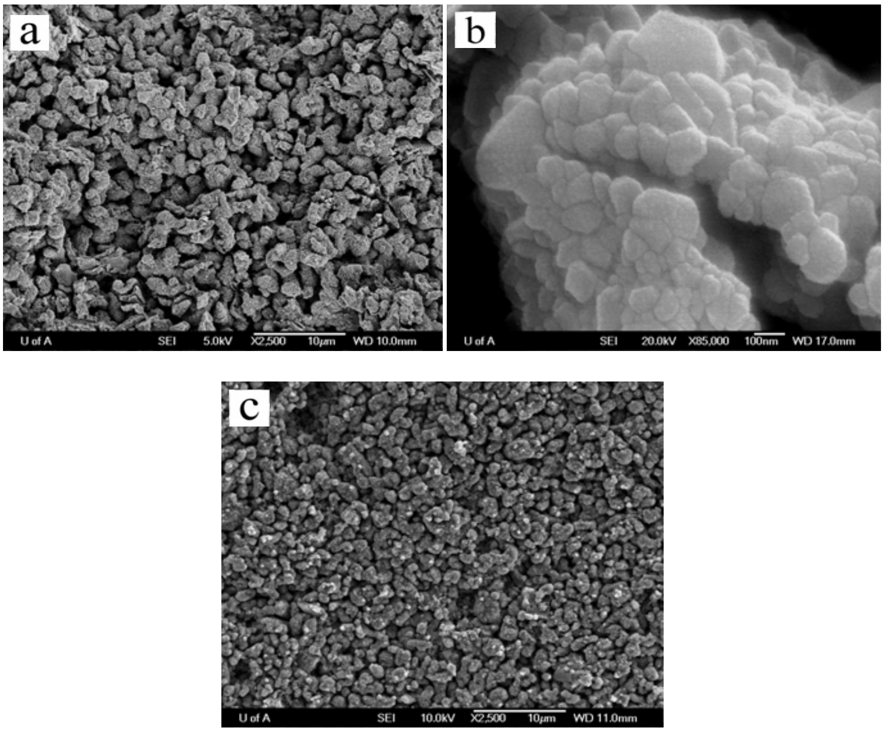

Figure 8 Morphologies of chromium oxide specimens after 100 hours exposure to SCW (625°C, 25~30 MPa): (a) low mag. (b) high mag; (c) sample with 5 wt. % added yttria after 600 hours SCW test.

The chromium oxide + yttria coupons exhibited much better stability than the pure chromium oxide ceramics in SCW environments as shown in Table 4. The weight change ratio measured for the samples with added yttria at 5 wt. % was less than 0.001 after 600 hours cyclic exposure in SCW at 625°C. It is obvious that adding yttria can improve the corrosion resistance of the chromium oxide based ceramics in SCW environment. The effect of adding yttria may be attributed to the reactive element effect. The large radius Y atom may segregate to the grain boundary, reducing lattice distortion and increasing the stability of the grain boundary, which can increase the stability of chromium oxide based ceramics in SCW.

4. Conclusion

The present results of corrosion tests for porous chromium carbide/oxide based ceramics in SCW reveal that porous chromium oxide possesses better corrosion resistance than porous chromium carbide. The porous chromium carbide was disintegrated by oxidation when the temperature of SCW was above 425°C. Porous chromium oxide samples show better corrosion resistance than porous chromium carbide, but partially disintegrated in SCW at around 625°C. Chromium oxide ceramics with added yttria exhibited much better corrosion resistance compared with the pure chromium carbide/oxides. The porous chromium oxide sample with 5 wt % added yttria exposed in SCW at 625°C for 600 hours shows no evident weight changes, revealing that adding yttria can improve the stability of chromium oxide ceramics in SCW environments.

Acknowledgements

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