PERFOMANCE EVALUATION OF THE CORROSION PERFOMANCE OF SEVERAL ODS STEELS EXPOSED TO SUPERCRITICAL WATER

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Abstract

Oxide-dispersion strengthened (ODS) steels are being considered as candidate alloys for use as primary fuel cladding material in the CANDU-SCWR. ODS steels show improved creep and radiation resistance, which make them promising candidates for the in-core applications in SCWRs. ODS alloys of austenitic stainless steels are also believed to have superior creep properties over their non-ODS counterpart materials. The supercritical water test loop at the University of New Brunswick has been used to test several ODS steels under supercritical water conditions (500°C, 25 MPa, deaerated). The steels that were prepared by ODS processing at the Beijing University of Science and Technology were two 14% Cr steels with different minor alloying elements, one 18% Cr steel, and one 304 commercial austenitic stainless steel. The base steels were atomized, mechanically alloyed with 0.35% Y_2O_3 and consolidated, to provide for oxide dispersion strengthening. The results of the loop exposure on these ODS steels are compared to those from previous experiments, where steels were of similar composition but not ODS processed.

Keywords: Materials, Corrosion, ODS Steel, CANDU-SCWR.

1. Introduction

As a signing member of the Generation IV International Forum, Canada is developing advanced nuclear systems for future use. One of the most promising designs is the CANDU-SCWR, a logical next step in the CANDU fleet. This proposed reactor design uses supercritical light water as coolant and is expected to operate with an outlet temperature of up to 625°C at 25 MPa. An increase in the operating temperature results in a considerable improvement in the thermodynamic efficiency when compared to conventional reactor designs. While the benefits of operating in the supercritical range are substantial, additional challenges are introduced by working in such an extreme environment. Research is being done to investigate materials, water chemistry and corrosion product transport under the aggressive conditions proposed for the CANDU-SCWR.

Several candidate materials are being considered for use in the CANDU-SCWR with several properties being targeted. In addition to corrosion and stress-corrosion cracking resistance, a suitable alloy must have low susceptibility to creep and irradiation damage, which can be issues in high-temperature nuclear environments. Stainless steels, nickel-based alloys and ferritic-martensitic (F/M) steels are alloy classes that are being considered for use in SCW applications. Thin oxide films with a tendency to spall have been observed on stainless steels exposed to SCW whereas thick, stable oxides are found on F/M steels after SCW exposure. In addition to base material design, coatings are being developed to enhance certain properties in order to meet the requirements of a SCWR. Both ceramic and metallic protective coatings have been prepared by a variety of techniques with varying degrees of success to date. Additional work needs to be done in the areas of film adhesion and oxide stability prior to implementation. In addition, coatings need to be developed along with alloy systems to ensure thermal, mechanical, and chemical compatibility.

Oxide-dispersion strengthened (ODS) steels are an emerging class of alloys in which a base alloy is processed into powder form, mechanically alloyed with nano-sized yttria powder and the mixture is consolidated by HIPing (hot isostatic pressing) or hot extrusion. This treatment enhances the creep strength and radiation resistance. In this study, several ODS steels have been tested in SCW to evaluate their corrosion resistance.

Austenitic stainless steels and nickel-based alloys are known to have low corrosion rates in SCW when compared to ferritic steels. However, stress corrosion testing using the CERT (constant extension rate tensile) technique on these austenitic alloys shows their susceptibility towards intergranular stress corrosion cracking. Experiments with ferritic alloys, like fossil plant steam tubing T91, have shown good resistance to stress corrosion cracking under SCWR conditions [1]. Ferritic steels have good resistance to irradiation damage, which causes swelling, however they are soft and do not retain the required strength at the temperatures proposed. ODS treatment imparts the desired high temperature creep resistance [2]. There is evidence that ODS treatment may improve also the corrosion resistance. A comparison between the oxidation behaviour of a 9% Cr ODS steel and two similar non-ODS ferritic steels showed that the ODS steel experienced less weight gain than the non-ODS steels, at all exposure times and temperatures, even though the ODS steel had a slightly lower bulk chromium concentration [3].

2. Experimental

To study the corrosion behaviour of several ODS steels arising from different precursor alloys, test coupons were exposed in supercritical water at 500^{o}C and 25 MPa. Exposure tests were carried out in a continuous flow loop in the Department of Chemical Engineering at the University of New Brunswick. Figure 1 shows a piping and instrumentation diagram of this system, which can operate under a range of operating conditions above and below the critical point of water. Deionized water from a reservoir (E-1) is pressurized with a positive displacement pump (P-1) to a pressure of 25 MPa. The water is initially heated with fluid returning from the system within a tube-in-tube interchanger (HX-1). Then water is heated through the critical point to the operating temperature of interest in the primary system heater (HX-2); for this study, a temperature of 500°C was used. The SCW then passes through an autoclave (E-2) in which the test coupons are suspended from a coupon tree for exposure. Following this autoclave, the hot fluid passes back through the tube-in-tube interchanger where some of its heat is transferred to the incoming water. Before returning to the reservoir, the fluid is brought to ambient conditions by passing through a chilled water cooler (HX-3) and a back-pressure regulating valve (BPRV-1).

Control systems are in place to monitor and regulate conditions within the system. Flow rate, temperature, pressure, oxygen concentration and conductivity are all recorded to a database using data acquisition software built in-house using Visual Basic. Test coupons were mounted on a coupon tree and placed inside the autoclave, Figure 2. These coupons were exposed to SCW within the autoclave for increasing exposure durations, up to 500 hours, to allow for SEM and weight change analyses to be carried out as a function of exposure time.

Several ODS materials were prepared by Dr. Ge’s group at the Beijing University of Science and Technology. Off-cuts were supplied to CANMET for metallographical characterisation (some of these are discussed in another paper by Li et al in this symposium) and to UNB for exposure testing in SCW. Corrosion test coupons of various dimensions (nominally 15x10x2 mm) were prepared from each sample by wire EDM. Prior to exposure the individual coupons were polished to 800-grit SiC finish, degreased with acetone and weighed and dimensioned. The composition of each alloy is shown in Table 1.

Four coupons cut from each of these five steels (two 14%Cr steels with varying alloying elements, an 18%Cr steel, a commercial 304-series SS that were atomized and ODS processed, and a non-ODS processed 12%Cr ferritic steel with tantalum and vanadium) were exposed to SCW at 500^{o}C and 25 MPa for durations of 100, 250 and 500 hours. All of the coupons were weighed and dimensioned before and after exposure to obtain weight change data corresponding to exposure time. Additionally, the coupon surfaces were characterized using SEM and EDS before and after the loop exposure and one coupon of each type was removed from the loop at each shut-down for surface characterisation. For this experiment, the flow rate in the loop was held constant at 100 g/min with the dissolved oxygen concentration maintained under nominally deaerated conditions; the oxygen concentration was measured using an Orbisphere EC oxygen sensor in the water purification circuit. It was maintained between 5 – 15 ppb for the first 250 hours of exposure but increased up to 75 ppb during the final 250 hours due to an unknown source of oxygen ingress.

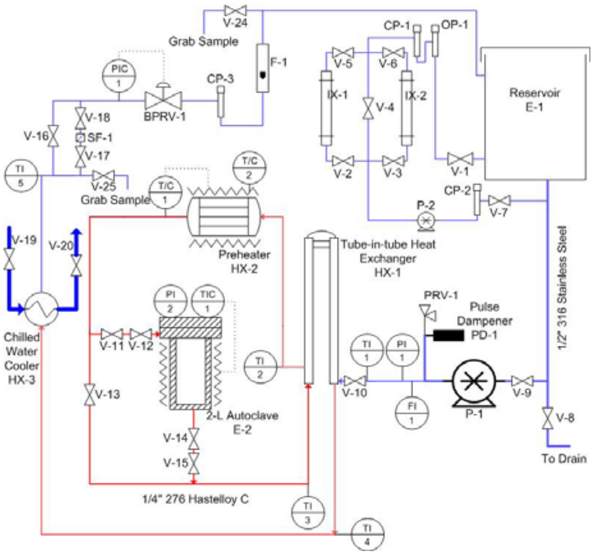


Figure 1- Schematic of UNB's SCW test loop.

Figure 2- Coupon tree.

Table 1. Nominal composition of ODS alloys tested in SCW.

Sample Designation	**Nominal composition***											
	Cr	**Ni**	**C**	**W**	**Si**	**Al**	**Mo**	**Mn**	**Ta**	**V**	**Ti**	**Y_2O_3**
14Cr-ODS#1	14	--	N/A	--	--	--	1	--	--	--	0.5	0.35
12Cr-NA#2	12	--	0.13	1.2	0.2	--	--	0.5	0.08	0.18	--	--
14Cr-ODS#3	14	--	0.06	1.8	0.2	--	--	--	--	--	0.5	0.35
18Cr-ODS#4	18	--	0.02	1.8	0.2	4	--	--	--	--	0.5	0.35
304SS-ODS#5	17.8	7.8	N/A	--	--	--	1	--	--	--	0.5	0.35

*note: balance Fe

3. Results and Discussion

For this experiment all of the coupons were exposed to SCW at 500°C for increasing times up to 500 hours. Weight change results were collected at intervals of 100, 250 and 500 hours to generate trends as a function of exposure time. Scanning electron microscopy examination, including EDS, was completed on all of the coupons. The weight change data for the four ODS steels along with the 12%Cr non-ODS material is shown in Figure 3. These data are compared with several non-ODS alloys that were previously tested at UNB under similar experimental conditions. The non-ODS comparison alloys include a 14%Cr steel (specially prepared by CANMET), commercial P91 steel and commercial 304SS (each of these non-ODS alloys are denoted with a * in the legend).

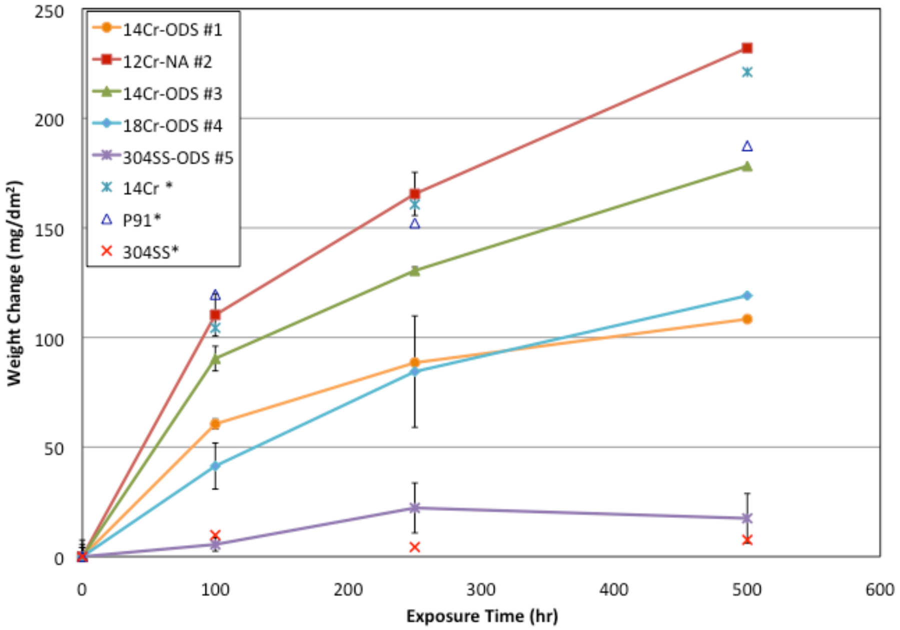
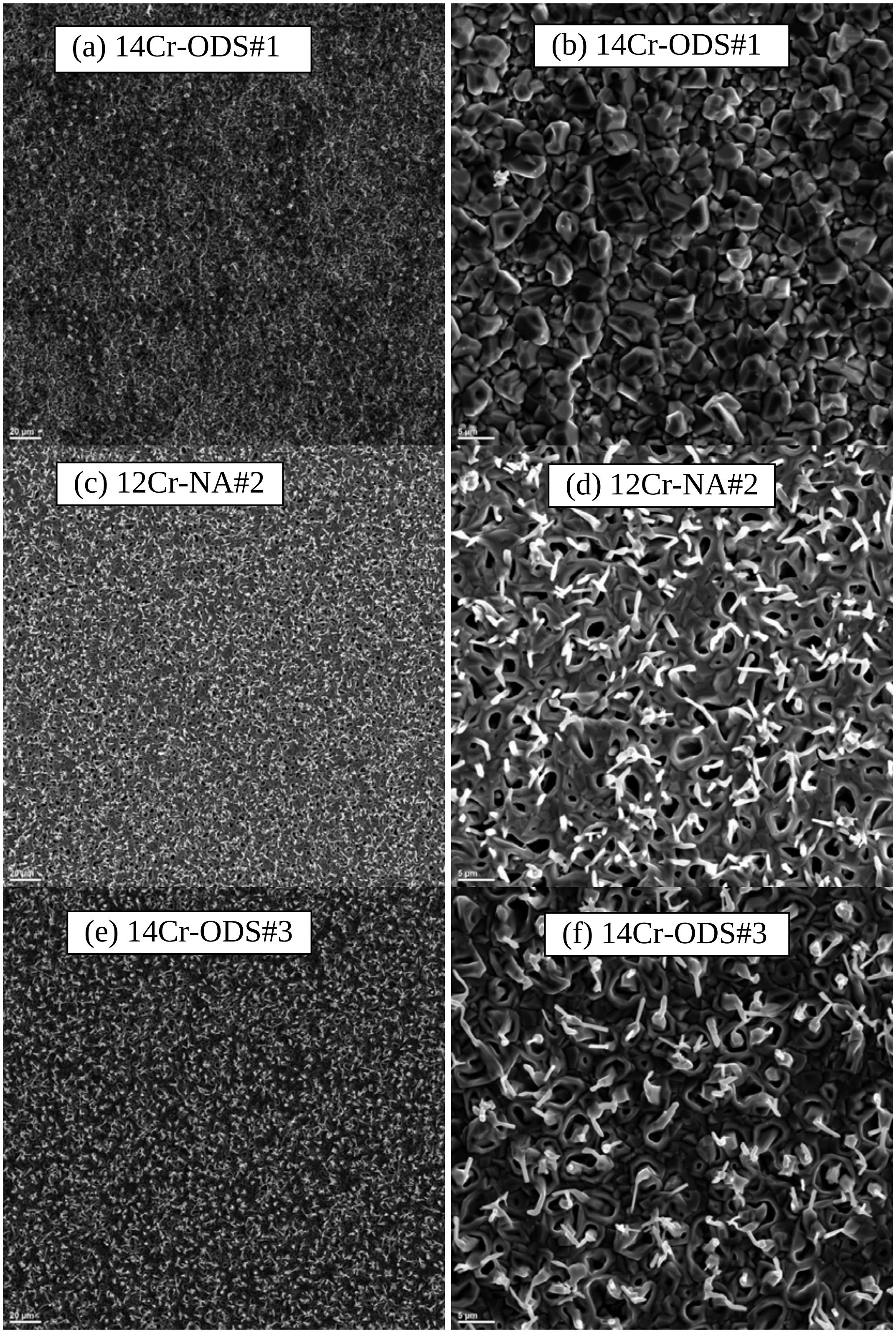


Figure 3. Weight change data for samples exposed to SCW at 500°C and 25 MPa.

The weight gain kinetics observed in Figure 3 are typical of steels and alloys undergoing high temperature oxidation. Initially, parabolic kinetics dominate but can transition to linear kinetics after a critical oxide thickness is surpassed [4]. This behaviour is attributed to an initial startup phase that follows diffusion-controlled parabolic growth kinetics as the oxide film develops. After some time, the corrosion rate stabilizes and weight gain increases linearly with time representing a steady oxidation or corrosion rate. This applies for alloys #1-4 with the austenitic stainless steels following simple linear kinetics at a much lower overall rate. The transition from the initial parabolic kinetics to linear kinetics seems to occur at or before 100 hours for samples #1-3 (low Cr alloys); a delayed transition for steel #4 (18%Cr ferritic ODS steel) to around 250 hours of exposure is attributed to the higher Cr content, although it is clear that the austenite phase present in the 304SS samples offers further oxidation resistance.

The 304SS-ODS samples experienced the smallest weight gain of any of the coupons that were tested in this run; the corrosion rate for 304SS-ODS was comparable to that of the 304SS commercial steel tested previously. Steel #2, the 12Cr-NA samples, exhibited the largest weight gain, with a similar magnitude to the 14Cr* and P91* samples from the earlier tests. The two 14Cr-ODS materials and the 18Cr-ODS material had intermediate weight changes, demonstrating the effect of increased Cr level in the alloys. The 14Cr-ODS #3 samples experienced nearly double the oxidation of the 14Cr-ODS #1 samples; the presence of molybdenum in the #1 sample (or its absence in steel #3) could account for this difference as the presence of Mo in the alloy can affect the passivity of the alloy surface when immersed in SCW. Detailed surface characterization is underway to examine the differences in the oxide phases present to determine the origin of the effect. The weight change data presented here is supported qualitatively by SEM work carried out at the Microscopy and Microanalysis Facility at the University of New Brunswick. Figure 4 shows post exposure SEM images for steels #1-5 at two different magnifications. The scale bars are 20µm and 5µm for the left and right images, respectively.



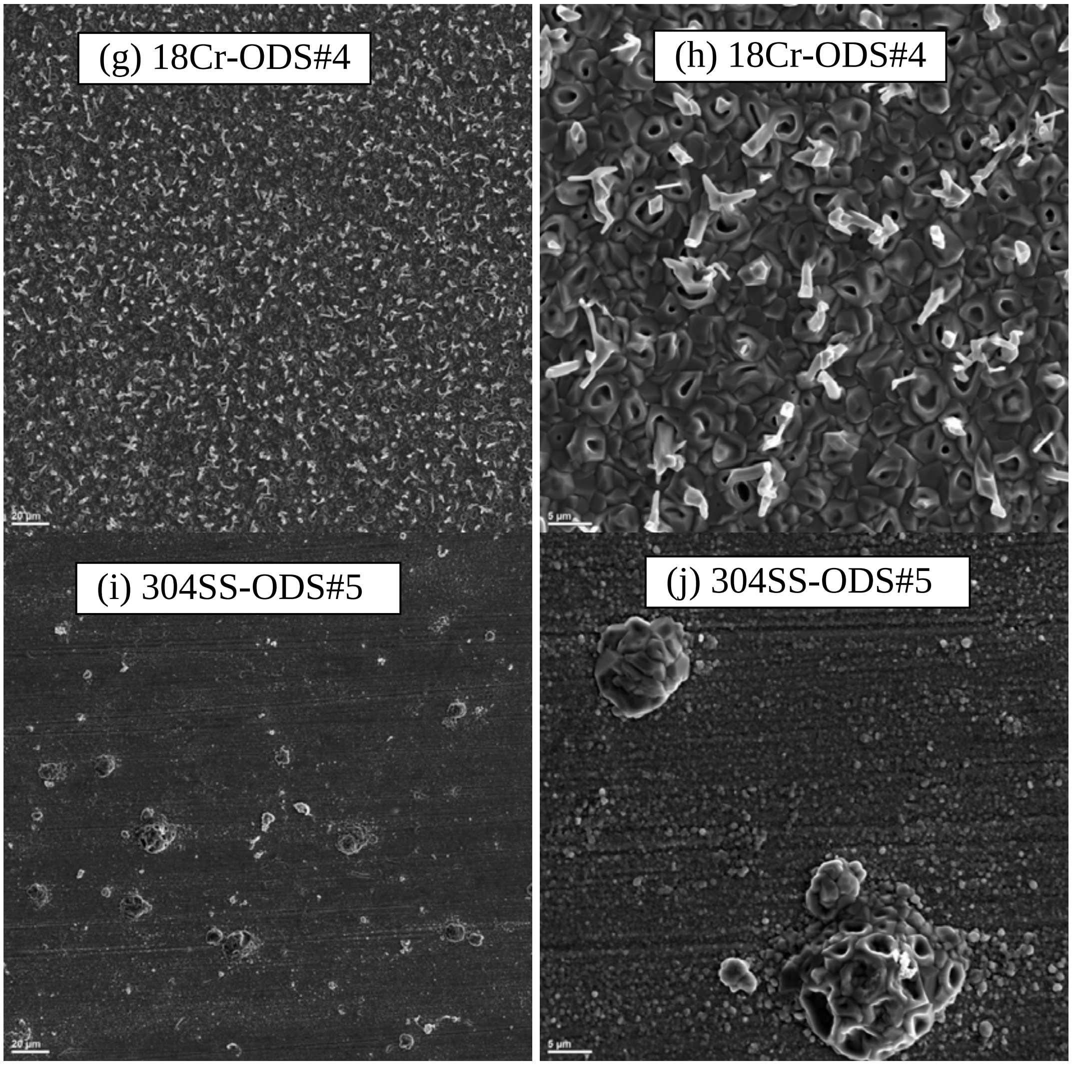


Figure 4. (a-j) Post exposure SEM images for ODS steels #1-5
(500 hours, 500°C, 25 MPa)

Figure 4 (a,b) shows the 14Cr-ODS #1 coupons after 500 hours of exposure to supercritical water at 500°C and 25 MPa. A well-developed continuous oxide film covers the entire coupon surface; EDS showed this to be an iron oxide, presumably magnetite. The tubular oxide morphology has been observed in previous tests and has been discussed in detail elsewhere [5-8]. Figure 4 (c,d) and (e,f) reveal post exposure SEM for the 12Cr-NA #2 and 14Cr-NA #3 coupons after 500 hours. The oxides on these samples exhibit similar morphologies; weight change results for steels #2 and #3 were also very similar. These oxide films are predominantly porous magnetite as seen before; however, for these two materials, white needle-like crystals extend from the underlying layer of magnetite crystals. The needles are lighter in colour, suggestive of the presence of a different phase. While EDS is unable to provide phase information, the relative height of the iron and oxygen peaks suggests that the needles may be hematite. Further work needs to be done to characterize these features, which will facilitate a better understanding of the mechanism of oxide film formation in supercritical water.

Steel #4, 18Cr-ODS (shown in Figure 4 (g,h)), experienced less weight gain than the first three materials. White needle-like features are again evident across the coupon surface, as on steels #2 and #3. The needles observed in Figure 4 (g,h) are sparsely distributed across the surface. While a similar mechanism may be at work, slight differences in the morphology of the oxide film and weight change kinetics could be related to additional protection resulting from increased chromium content in steel #4. Finally, Figure 4 (i,j) shows SEM images for 304SS-ODS #5 after 500 hours of exposure. Weight gains for the stainless steel were well below those for steels #1-4 and this is clearly revealed by the SEM. Very little oxidation has occurred across the coupon surface; nodules of the tubular-magnetite are distributed on the coupon with most of the surface unaffected. In fact, pre-exposure polishing lines are still visible in Figure 4(j). The localized growth of the nodules is typically attributed to surface defects associated with grain-boundaries and has been seen before on austenitic alloys [8, 9].

The presence of the white needle-like crystals is interesting. They appear to grow off of the lower tubular magnetite substrate, potentially fed by iron diffusing through the holes and porosity in the primary oxidation layer. The fact that they may be hematite and not magnetite is reflective of the higher dissolved oxygen concentrations present during the later stages of the test. In fact, SEM images of the samples removed from the earlier durations of the test contain few (or no) crystals of this sort (Figure 5 (a-e)). Further testing and characterization of these steels with varying concentrations of dissolved oxygen in the SCW are needed to evaluate their oxidation tendencies under a wider range of conditions.

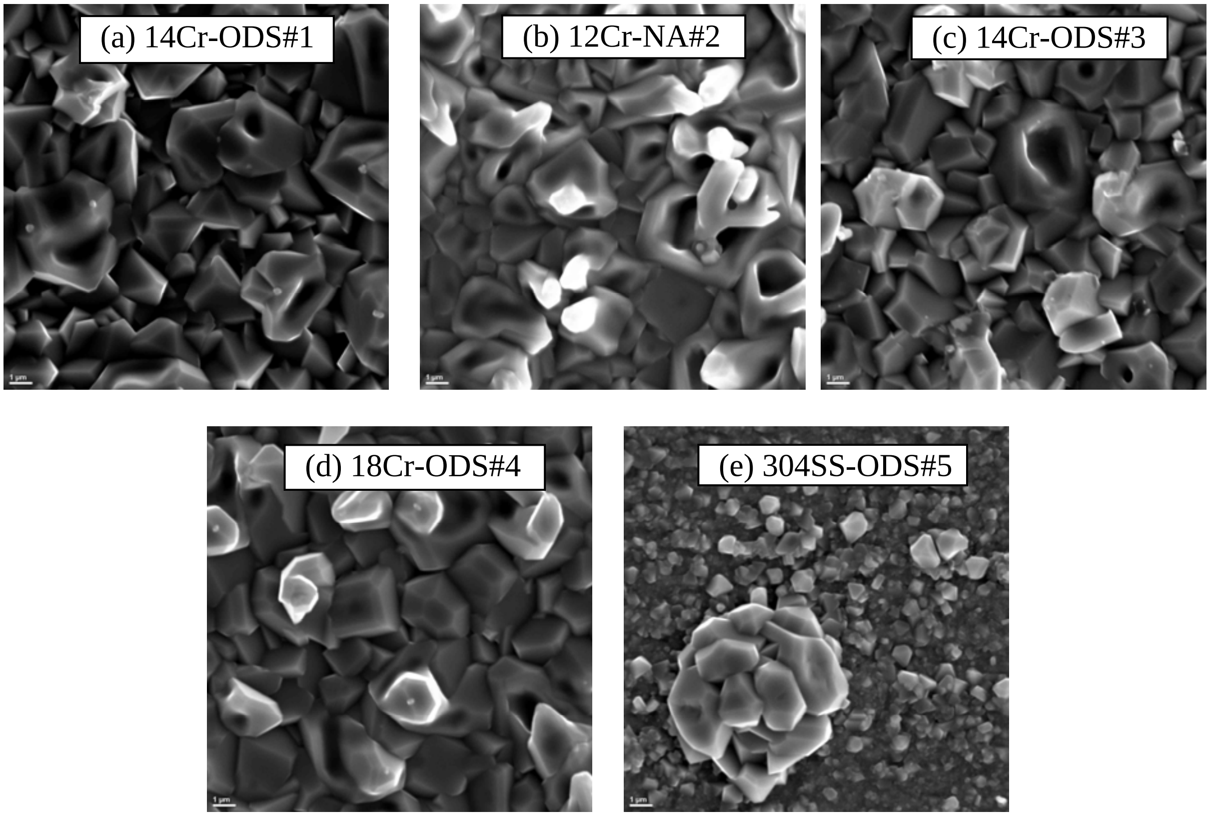


Figure 5 (a – e). SEM images for ODS steels #1-5 (250 hours, 500^{o}C, 25 MPa)

4. Conclusion

In this study, four steels with varying compositions underwent ODS processing. A 12% chromium steel (non-ODS) along with coupons cut from the four ODS steels were exposed to supercritical water at 500^{o}C and 25 MPa for durations of up to 500 hours in the flow loop at the University of New Brunswick. Weight change results were obtained at increasing time intervals, up to 500 hours, and the plan views of coupons after exposure have been observed under SEM. The 12Cr-NA steel experienced the most weight gain and had a similar oxide morphology to one of the 14Cr-ODS alloys. The ODS-processed 304SS showed the most resistance to corrosion with only small magnetite nodules observed sporadically across the coupon surface. All of the ODS steels experienced better protection than the non-ODS materials; in the case of alloys with 14% Cr, the ODS alloy with 1% Mo showed visibly better corrosion resistance than the Mo-free alloy. The exact mechanism of this difference is being investigated in on-going work.

5. Acknowledgements

The authors thank the NSERC/NRCan/AECL Generation IV Technologies Program for funding. The Canadian Foundation for Innovation (CFI) and the New Brunswick Innovation Foundation (NBIF) are thanked for funding the construction of the test loop.

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