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Austenitic Stainless Steels and Alloys With Improved High-Temperature Performance for Advanced Microturbine Recuperators

**Philip J. Maziasz, Bruce A. Pint, John P. Shingledecker,
Karren L. More, Neal D. Evans, and Edgar Lara-Curzio**
Oak Ridge National Laboratory
Metals and Ceramics Division
Oak Ridge, TN 37831-6115
Phone: (865) 574-5082, e-mail: maziaszpj@ornl.gov

ABSTRACT

Compact recuperators/heat-exchangers increase the efficiency of both microturbines and smaller industrial gas turbines. Most recuperators today are made from 347 stainless steel and operate well below 700°C. Larger engine sizes, higher exhaust temperatures and alternate fuels all demand recuperator materials with greater performance (creep strength, corrosion resistance) and reliability than 347 steel, especially for temperatures of 700-750°C. The Department of Energy (DOE) sponsors programs at the Oak Ridge National Laboratory (ORNL) to produce and evaluate cost-effective high-temperature recuperator alloys. This paper summarizes the latest high-temperature creep and corrosion data for a commercial 347 steel with modified processing for better creep resistance, and for advanced commercial alloys with significantly better creep and corrosion resistance, including alloys NF709, HR120. Similar data are also provided on small lab heats of several new ORNL modified stainless steels.

INTRODUCTION

Microturbines are attractive for distributed generation (DG), combined heat and power (CHP), and possibly combined cycle (microturbine-fuel cell) applications. Microturbines are ultraclean, relatively quiet, and fuel flexible. The advantages of DG were clearly seen during the Blackout of 2003 that affected the Midwestern and the Northeastern U.S., and microturbines may have a growing role in the power portion of various homeland security strategies [1]. Recuperators are compact heat exchangers that are necessary for high-efficiency advanced microturbines [2-4], but are also a costly and challenging component of such microturbine systems. Most recuperators are currently made from 347 stainless steel, but as increased efficiency drives turbine exhaust (and hence recuperator inlet) temperatures up, they will have to be manufactured from heat- and corrosion-resistant stainless steels and alloys with more capability and durability at higher temperatures. Economics are pushing microturbine engine sizes up from 30-70 kW to 200-250 kW, and some applications will demand cyclic rather that steady service conditions[5,6], which further challenges recuperator performance.

The Department of Energy (DOE) has an Advanced Microturbine Program [4] with the goal to design and build microturbines with efficiencies of 40% or more. Recuperators with upgraded temperature capability and performance are an enabling technology toward this goal. While there are various types of compact recuperators [2,7], the main types used on commercial microturbines today are the primary surface (PS) welded air cells (Solar Turbines, Inc. design) in an annular recuperator configuration used by Capstone Turbines [5], Inc., and the brazed plate and fin (BPF) air cells in a stack recuperator configuration used by Ingersoll Rand Energy Systems [6]. The Oak Ridge National Laboratory (ORNL) has been conducting materials research and development in support of the Advanced Microturbines Program for several years to select, characterize and develop materials with improved high-temperature performance for recuperators [7-11]. Over the last year, ORNL has focused its efforts on a) characterizing the properties of current commercial 347 steel sheet and foil used to manufacture recuperator air cells; b) identifying advanced alloys and/or modified commercial processing for making recuperators with upgraded performance; c) developing lab-scale modified 347 steels that offer the most cost-effective improvements in performance and reliability relative to standard 347 steel; and d) understanding

the life-limiting mechanisms of actual engine-tested 347 steel recuperators. These same steels and alloys are also being tested in the ORNL Advanced Microturbine Test Facility, which is based on a modified Capstone 60 kW microturbine [12].

The value of these efforts on advanced materials for improved recuperator performance goes beyond microturbines, since recuperators are also used in industrial gas turbines and marine gas turbines [3,6,13]. Compact heat-exhangers are also important for other applications, including heat transfer or fuel reforming for fuel cells [3], and heat transfer in high-temperature gas-cooled nuclear reactors [14].

SUMMARY OF CREEP RESISTANCE OF COMMERCIAL HEAT-RESISTANT ALLOY FOILS AND SHEET

Previous initial screening work on a wide range of commercial or developmental heat- and corrosion-resistant alloys, processed as lab-scale foils at ORNL and creep tested at 750^oC and 100 MPa, established that HR120, and 625 alloys were the most cost-effective, high-performance recuperator alloy alternatives to 347 stainless steel. HR214 was identified as a possible higher cost material for recuperator service above 800^oC. Several demanding military recuperator applications employ alloy 625 for both PS and BPF air cells [3,13]. Commercial alloy compositions are given in Table 1. Experimental details regarding ORNL lab-scale foil processing to make 0.1 mm thick foils, microcharacterization and creep-testing have been given elsewhere [8].

In the past year, commercial 0.09 mm foil of HR120 alloy was obtained from Elgiloy Specialty Metals and tested for comparison to various foils and sheets of standard 347 steel used for commercial recuperator manufacturing. The modified alloy 803 was part of a small-scale development project between ORNL and Special Metals, Inc., but that alloy is not available commercially, so it is not included in this study at this time. Boiler tubing of NF709 stainless steel (Fe-20Cr-25Ni,Nb,N, see Table 1) from Nippon Steel Corp. was split, flattened and then also processed into foil for corrosion studies. In plate or tube form, NF709 is one of the most creep-resistant austenitic stainless at $700-800^oC$ [15,16]. Therefore it was also included in these most recent ORNL creep studies of foils for advanced recuperators.

The results of creep-rupture tests in air at 750^oC and 100 MPa on HR120 and NF709 are shown in Fig. 1, with previous data on similar foils of alloy 625 and HR214 included for comparison. Foils of both HR120 and NF709 alloys have much better creep-rupture resistance than standard, commercial 347 stainless steel foil at this 750^oC creep condition. The NF709 foil has about 1.67 times longer rupture life, and slightly more ductility with a lower secondary creep rate, but is otherwise still comparable to the HR120 alloy. Both alloys have more than double the creep-rupture ductility of alloy 625 and HR214. Both alloy 625 and HR214 have much lower creep rates, and hence much longer life for components limited to 5-10% creep, but the rupture life of the NF709 compares favorably to both alloys. If the NF709 alloy were commercially available as foil at less than 3 times the cost of 347 steel, it would be the most cost effective advanced recuperator alloy tested to date.

NEW PROCESSING FOR IMPROVED CREEP-RESISTANCE OF STANDARD, COMMERCIAL 347 STAINLESS STEEL SHEETS AND FOILS

The recent ORNL program for upgrading the performance of commercial recuperator components began with establishing baseline creep behavior for the various commercial 347 stainless steel foils and sheets used by original equipment manufacturers (OEMs) for manufacturing recuperators. That initial work showed significant variability in the creep-rupture lives of standard, commercial foils and sheets of standard 347 steel (from 0.076 to 0.254 mm in gage thickness) at 700-750^oC, ranging from 50 to 500 h at 704^oC and 152 MPa, with rupture ductilities from 3 to 27% [7,11]. These results clearly established a need for adjusting the processing for consistently better properties, so that a joint project between ORNL and the Allegheny Ludlum Technical Center (C. Stinner, PI) was established to produce commercial scale quantities of 0.076, 0.1, 0.127 mm foils and 0.254 mm sheet (the most common products used to manufacture PS or BPF recuperator air cells), with the processing parameters adjusted for improved creep-resistance. The steel with more creep-resistant processing is now designated AL347HP^{TM} [17], and is commercially available from Allegheny Ludlum. More details on the overall effort and results are given elsewhere by Stinner [17].

The effect of modified processing on the creep resistance of 0.076 mm foil and 0.254 mm sheet at 704^oC and 152 MPa is shown in Fig. 2. The 347 steel with standard processing is designated T347, while the same heat of 347 steel with modified processing is designated AL347HP (high performance). The AL347HP shows about a 50% improvement in rupture life for 0.076 mm foil, and a 39% improvement for 0.254 mm sheet, relative to T347 tested at 704^oC, and both still show about 30-36% improvement after creep at 750^oC and 100 MPa. The AL347HP shows much larger improvements for similar testing of 0.1 and 0.127 mm foils. At 704^oC and 152 MPa, improvements ranged from 8-14.5 times longer rupture life of the AL347HP. Creep strain curves for 0.127 mm foils are shown in Fig. 3. Similar improvements for AL347HP still persist for creep at 750^oC and 100 MPa, as shown in Fig. 4, but the secondary creep rates and rupture ductilities are higher than at 704^oC.

The modified processing for AL347HP steel involved using higher temperatures on the continuous annealing line used for the foils and sheets in order to achieve the desired microstructural targets of a moderately coarser grain size and dissolution of NbC precipitates during annealing [17]. Figure 5 compares as-processed 0.1 mm foils, and shows that T347 steel has a bimodal grain size, with many small grains mixed in among larger ones. Part of the creep resistance of the AL347HP comes from processing that removes all of the fine grains (most likely by coalescence) to produce a more uniform, coarser grain size that on average still remains below 20 μm. Transmission electron microscopy (TEM) analysis of the microstructure that develops within individual grains of such foils during creep at 704^oC is shown in Fig. 6. The AL347HP clearly has 100-1000 times more nanoscale NbC precipitates than T347 steel, which form during creep to make the grains stronger, which then helps lower the secondary creep rate and prolong the secondary creep regime. Although not shown here, the AL347HP also has less that 20% of the FeCr sigma phase found in T347, despite hundreds of hours longer creep

exposure [17]. This change in the overall precipitation behavior also helps extend the rupture life of the AL347HP.

This project concluded with commercial sizes and quantities of foil and sheet appropriate for manufacturing BPF recuperator air cells shipped to Ingersoll Rand Energy Systems, and of foil for manufacturing PSR recuperator air cells shipped to Capstone Turbines.

While creep resistance is one fundamental measure of improved temperature capability of foils for recuperator applications, resistance to moisture enhanced oxidation is another such fundamental measure, and the AL347HP is likely to have similar oxidation/corrosion resistance to the standard T347 because the nominal steel composition was not changed [18,19]. The coarser grain size of the AL347HP may also affect the formation of the protective surface oxide scale, but such effects must be determined by additional, systematic testing.

DEVELOPMENT OF NEW MODIFIED 347 STAINLESS STEELS WITH IMPROVED CREEP AND OXIDATION RESISTANCE

Advanced microturbine recuperators should be able to operate reliably at 700°C or slightly above, without sacrificing durability and lifetime (ie. up to 40,000 h), as well as withstand the higher pressure ratios in larger engines, more cycling without leaking or failure, and more corrosive fuels (flare gas, land-fill gas, biofuels, etc.). Commercially available alloy 625 meets or exceeds such performance requirements, but at 3.5 - 4 times the cost of 347 stainless steel. In fact, some high performance BPF recuperators are manufactured from alloy 625 [6]. Alloy HR120 is also commercially available and may also meet those requirements at a cost about similar to alloy 625. However, it would be very attractive to maximize the performance and temperature capability of the low-cost 347 steel. This has been the focus of alloy development efforts at ORNL for the last several years [3,7,11].

Several 15 lb heats of 347 stainless steel with modified compositions have been melted at ORNL and hot-rolled into plate, and then cold-rolled and annealed into 0.1 mm thick foils. The compositions of two promising heats of modified 347 steels and a related Fe-20Cr-20Ni stainless steel are given in Table 1 [20]. These modified 347 steels have nitrogen, manganese, and copper added to make the parent austenite phase more stable and stronger at higher temperatures; significantly, these elements do not increase the cost. As seen from Table 1, the combination of Nb and N in these new steels is similar to the strengthening additions found in HR120 and NF709, but the combination of Mn and Cu with Nb + N is unique. Several other advanced austenitic stainless steels for high-temperature fossil boiler tubing applications have been been developed by the Japanese (eg., super 304H, with Nb, N and Cu added) or the European COST 522 program (modified Esshette 1250, with N, Cu and W added) [21,22], but without the Mn addition that is unique to the ORNL steels. Table 2 illustrates different approaches to calculating Ni and Cr equivalents, Ni balance (Nibal) or % delta ferrite as measures of austenite stability, to help compare the various steels and alloys in Table 1. The combination of N, Cu and Mn makes the ORNL modified 347 steels behave as though they have much more added Ni (18-23% Ni by some of the calculations), or much more stable austenite phase (positive or higher Nibal number or 0% delta ferrite). The Fe-20Cr-20Ni steel compares well to the Ni equivalents or austenite stability of the NF709 composition (Fe-20Cr-25Ni).

Previous data on foils have shown improved creep rupture resistance of the ORNL modified 347 steels compared to standard 347 steel, for creep at 750°C and 100 MPa [7,11]. A similar relative comparison of the modified 347 steels creep tested at the same conditions, but in the form of wrought 0.76 or 1.52 mm thick plate, is give in Fig. 7. The MOD 2 steel exhibited about 2.5 times longer creep rupture life and the MOD 4 steels about 4.5 times longer life than standard 347 steel, mainly due to a prolonged secondary creep regime and much lower secondary creep rate. The creep resistance of the MOD 20/20 steel is not as good as the modified 347's, but it is still better than standard 347 stainless steel.

Even more important than the improvement in creep rupture resistance of the ORNL modified steels are the improvements in resistance to moisture-enhanced oxidation. While previous data showed a significant improvement in oxidation resistance up to 1000 h in 10% water vapor at 700-800°C [7,11], more recent results also have shown severe susceptibility to break-away oxidation of standard 347 steel in 10% water vapor at 650°C after only 1000-2000h. Figure 8 shows results of longer term testing at 650°C, in which most of the modified 347 heats showed almost the same good resistance to breakaway oxidation as found in NF709, HR120 and 625 alloys. While part of the improvement might be explained by the various alloying additions having the same effect as adding more Ni to the alloy [18], detailed microanalysis indicated a more direct role of the Mn addition in forming surface oxide scale [23,24]. Microanalysis of standard 347 and MOD 4 foils tested for 1000h at 700°C and 10% water vapor showed a stable, protective oxide scale on the MOD 4 steel, while the standard 347 steel exhibited the typical and rapid formation of Fe_2O_3/Cr_2O_3 that occurs during breakaway oxidation (Fig. 9). High resolution TEM microstructural and microcompositional analysis of the oxide scale on the MOD 4 specimen shows an outer layer of MnO_x above a mixed $(Mn,Cr)O_x$ layer, and an inner Cr-rich layer (Fig. 10). Surprisingly, there appears to be another mixed $(Mn,Cr)O_x$ layer adjacent to the substrate. If such an outer oxide layer is effective in reducing the rate of loss of the protective chromia scale by formation of the intermediate chromium oxy-hydroxides, then that may explain some of the beneficial effect of the Mn addition to the alloy, and confirms effects of Mn proposed by others [23]. Although longer time testing is necessary at 650-750°C, the combination of improved creep resistance and improved resistance to moisture enhanced oxidation makes the new ORNL modified 347 stainless steels attractive candidates for commercial scale-up as cost-effective recuperator alloys with higher temperature performance.

CONCLUSIONS

Alloys 625 and HR120 are commercially available sheet and foil materials with significantly better oxidation and creep-resistance than standard commercial 347 steel at 650-750°C, for enhanced performance and temperature capability of recuperators at about 3.5-4 times the cost of 347 steel. The NF709 (or similar Fe-20Cr-25Ni-Nb,N steel) and new ORNL modified 347 steels (containing Mn, N and Cu) also have the potential to be more cost-effective alloys with upgraded performance and temperature capability for such recuperator applications, but they are not yet commercially available.

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Table 1 – Compositions of Heat-Resistant Austenitic Stainless Alloys Processed into Foils at ORNL (wt.%)

Alloy/vendor	Fe	Cr	Ni	Mo	Nb	C	Si	Ti	Al	Mn	Others
				Commercial stainless steels, alloys and superalloys							
T347 steel	69.5	17.8	9.4	0.25	0.63	0.042	0.71	-	-	1.54	0.13 Co
NF 709	51	20.5	25	1.5	0.26	0.067	0.4	0.1	-	1.03	0.16 N
HR 120	39	25	32.3	1	0.7	0.05	0.6	0.1	0.1	1	0.3 Co, 0.2 N, 3 W max
HR 214	3.0	16	76.5	-	-	-	-	-	4.5		+ minor Y
alloy 625 (Special Metals)	3.2	22.2	61.2	9.1	3.6	0.02	0.2	0.23	0.16	-	
				ORNL developmental stainless steels							
Mod. 347-2	58.7	19.3	12.6	0.25	0.37	0.029	0.36	-	0.01	4.5	0.25 N, 4 Cu
Mod. 347-4	61.2	19.3	12.5	0.25	0.38	0.03	0.38	-	0.01	1.8	0.14 N, 4 Cu
Mod. 20/20	52.7	20.9	20.2	0.3	0.25	0.09	0.25	-	0.01	4.8	0.17 N, 0.3 Cu

n.a. – not available

Table 2 – Calculations of Relative Austenite Phase Stability Based on Alloy Composition

Ni-Cr Equivalents for Austenitics							
Alloy	Heat#	Ni_{eq}^{A}	Cr_{eq}^{A}	Ni_{eq}^{B}	Cr_{eq}^{B}	Nibal	δ (%)
Std. 347		11.4	20.2	11.4	19.0	-2.90	13
NF709		31.4	24.1	32.2	22.7	12.92	0
HR120		39.6	30.0	40.3	27.3	14.84	0
MOD 2 (Mod. 347)	18115	23.2	21.1	23.2	20.3	7.27	0
MOD 4 (Mod. 347)	18116	19.0	21.2	18.5	20.3	2.48	0
MOD 20/20	18529	29.7	22.3	30.4	21.7	12.50	0

$Ni_{eq}^{A} = Ni+Co+0.5Mn+30C+0.3Cu+25N$

$Cr_{eq}^{A} = Cr+2Si+1.5Mo+5V+5.5Al+1.75Nb+1.5Ti+0.75W$

$Ni_{eq}^{B} = Ni+0.5Mn+30(C+N)$

$Cr_{eq}^{B} = Cr+Mo+1.5Si+0.5Nb$

Nibal = $Ni_{eq}^{B} - 1.36Cr_{eq}^{B} + 11.6$

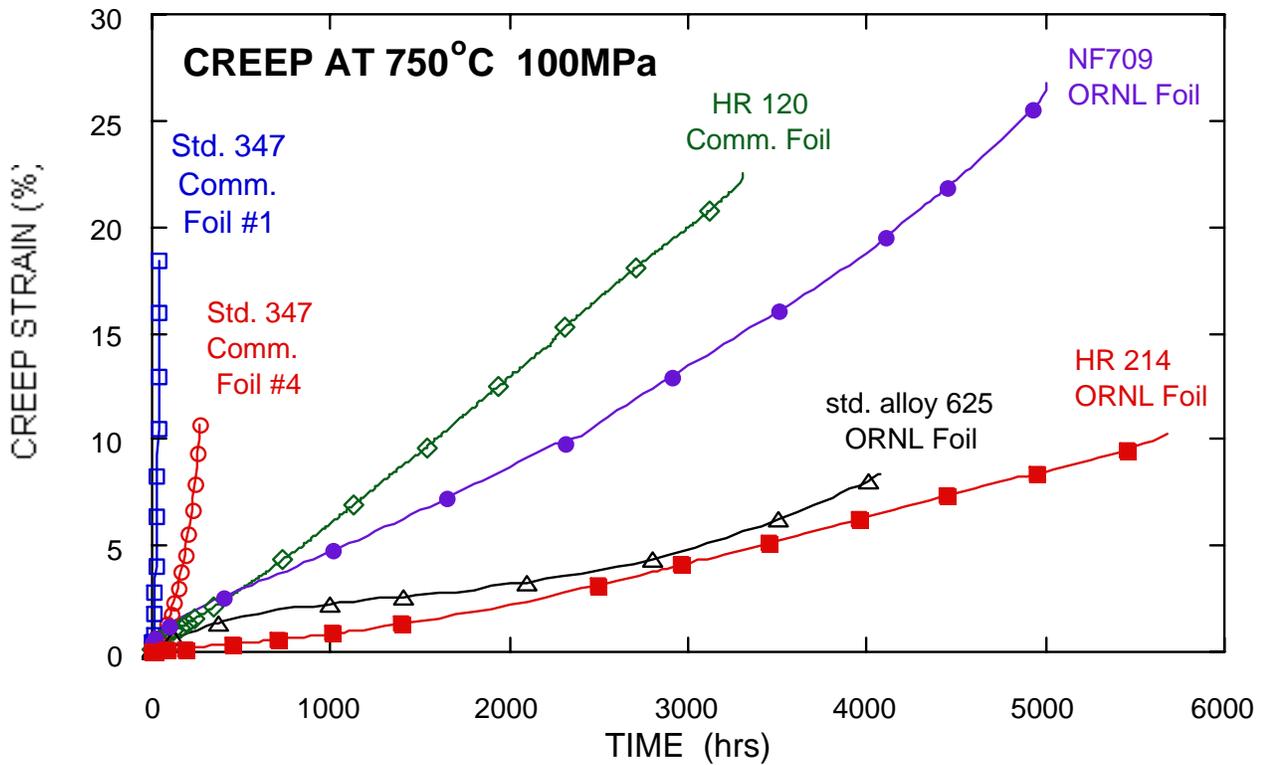δ from Schaffler-type Diagram (ASME Section VIII - Div. 1)

Figure 1 – Plots of creep strain versus time for creep rupture testing in air at 750°C and 100 MPa of foils (0.076 to 0.1 mm thick) of the various commercial heats of 347 austenitic stainless steels, stainless alloys or Ni-based superalloys. Designations also include whether the tests were of commercial foils or of foils processed on a lab-scale at ORNL.
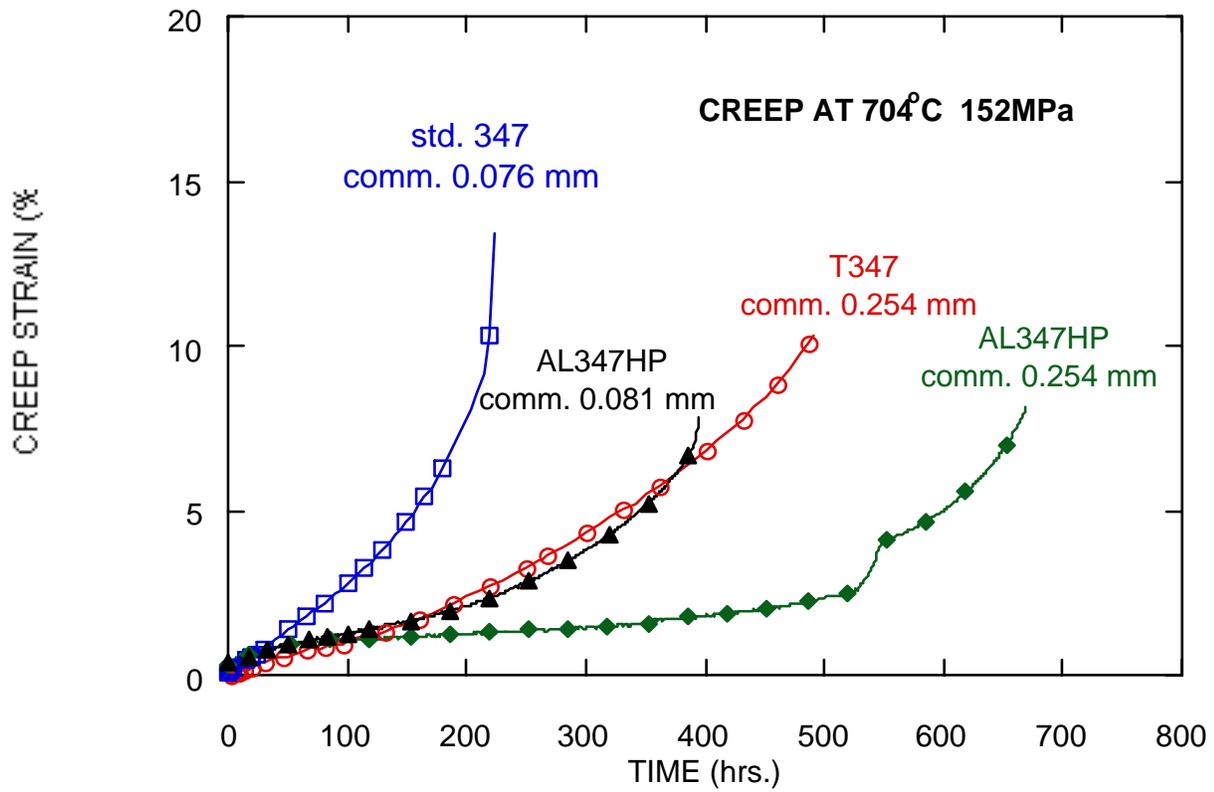
Figure 2 – Comparison of creep strain versus time curves for commercial recuperator foils (0.076 and 0.081 mm) and 0.254 mm sheet of standard 347 stainless steel tested at 704°C and 152 MPa in air. AL347HP specimens had modified processing for increased grain size and carbide dissolution, which improves the creep resistance.
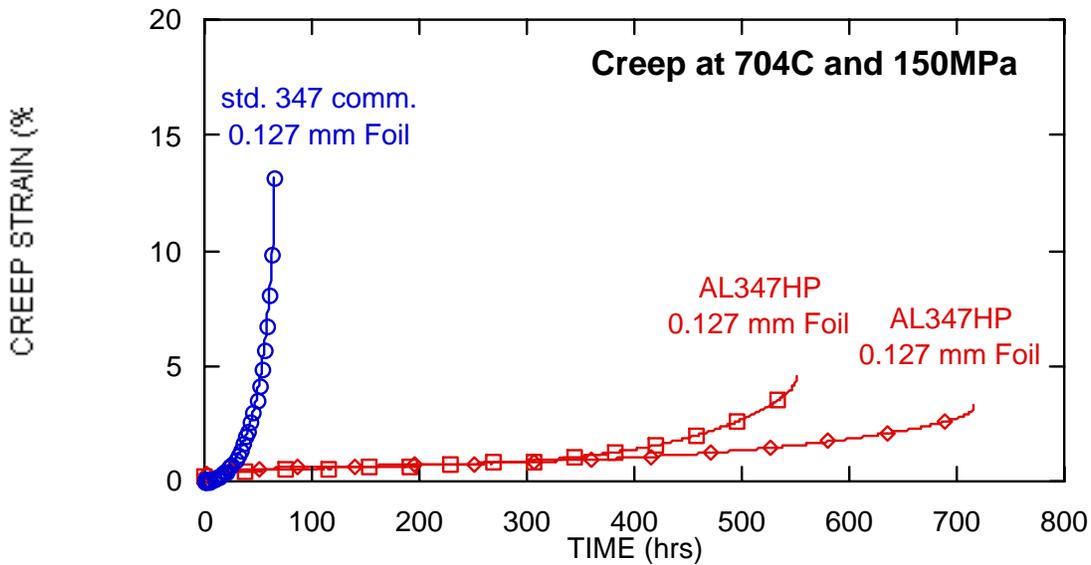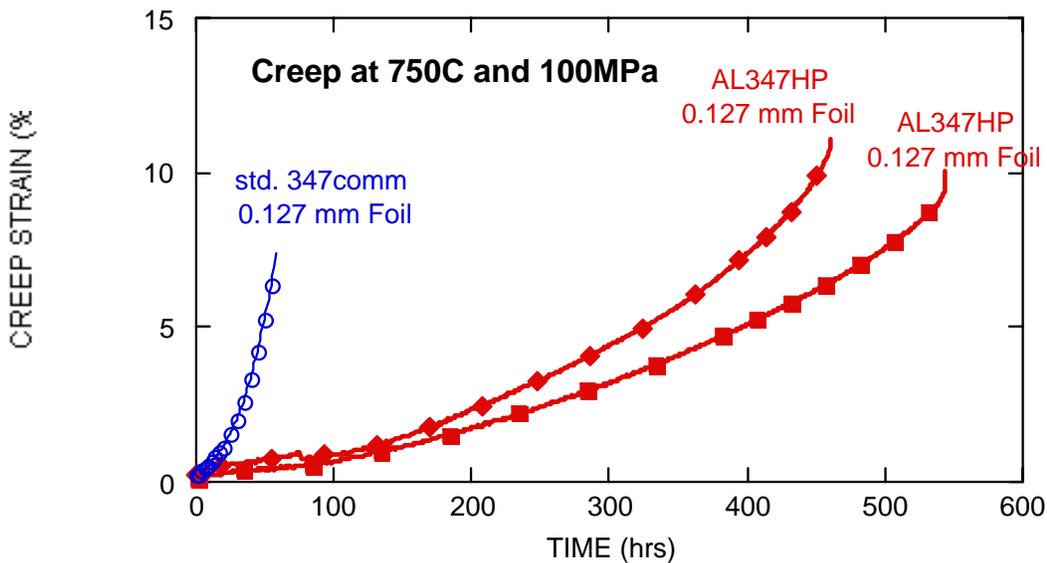
Figure 3 – Comparison of creep strain versus time curves for commercial 0.127 mm recuperator foils of standard 347 stainless steel tested at 704°C and 152 MPa in air. AL347HP specimens had modified processing for increased grain size and carbide dissolution, which improves the creep resistance.

Figure 4 – Comparison of creep strain versus time curves for commercial 0.127 mm recuperator foils of standard 347 stainless steel tested at 750°C and 100 MPa in air. AL347HP specimens had modified processing for increased grain size and carbide dissolution, which improves the creep resistance.

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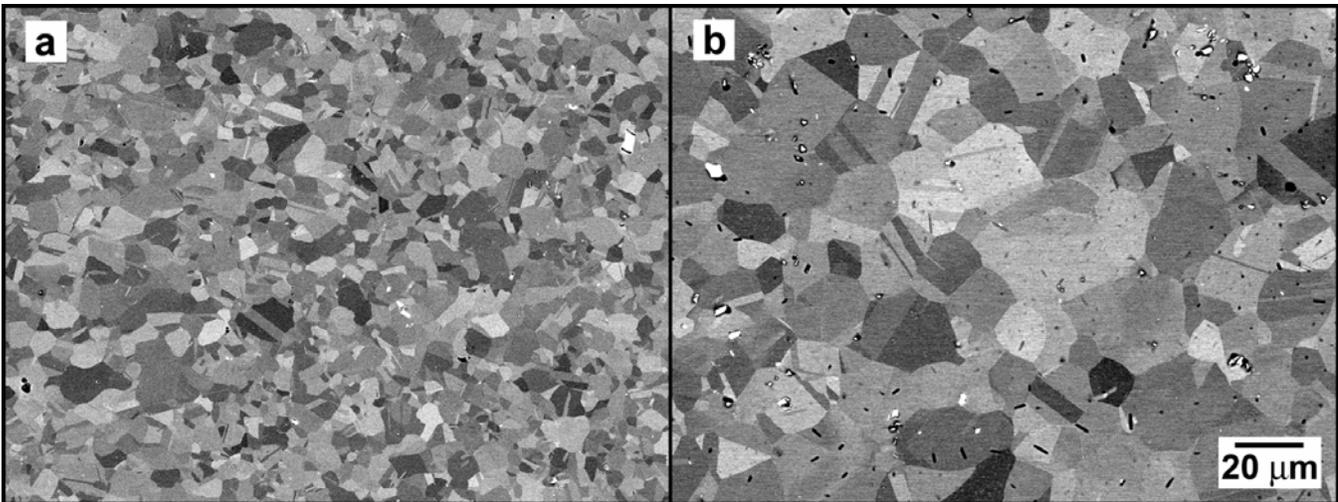
Figure 5 - Comparison of as-processed grain size for commercial 0.1 mm recuperator foils of standard 347 stainless steel with a) standard processing and b) modified processing (AL347HP). The AL347HP specimen had modified processing for increased grain size and carbide dissolution. Grain size is viewed by back-scattered electron (BSE) imaging of electropolished TEM discs in a scanning electron microscope (SEM).
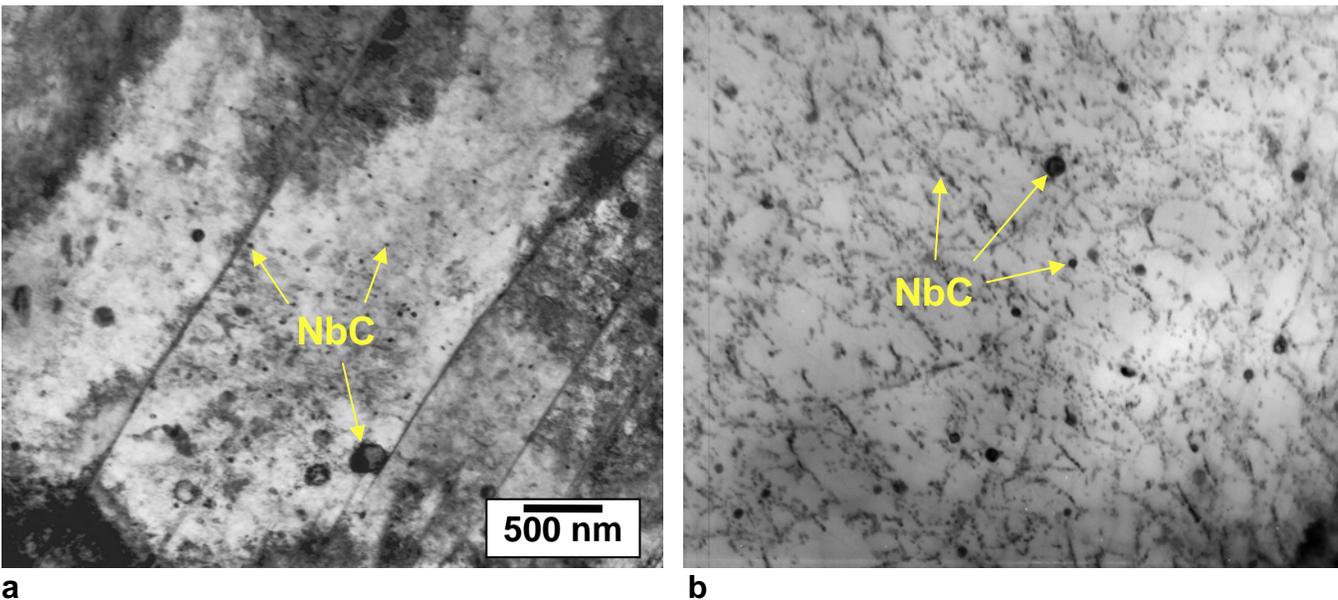

Figure 6 - Comparison of the intragranular fine carbide precipitation for commercial 0.1 mm recuperator foils of standard 347 stainless steel with a) standard processing and b) modified processing (AL347HP) after creep-rupture testing in air at 704°C and 152 MPa. The standard T347 steel ruptured after 51.4 h, while the AL347HP ruptured after 401.2 h. The AL347HP specimen formed many times more nanoscale NbC precipitates, which provide the improved creep resistance. Nanoscale NbC dispersions are viewed by transmission electron microscopy (TEM) imaging of electropolished discs.
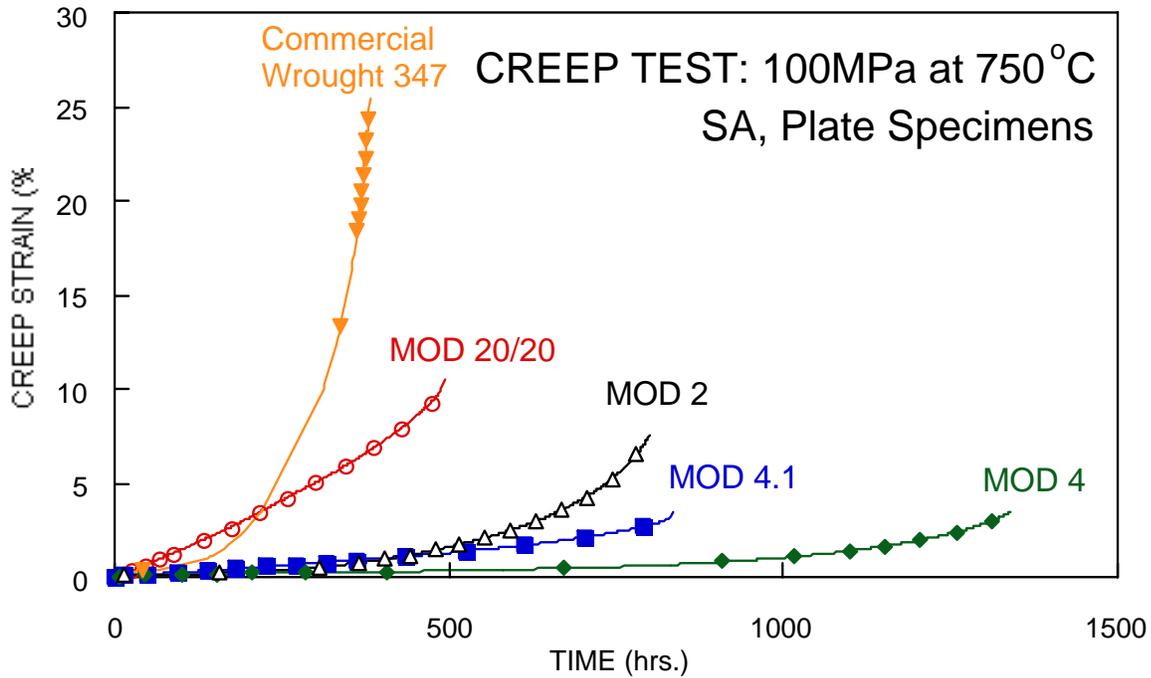
Figure 7 – Plots of creep strain versus time for creep-rupture testing of standard commercial and ORNL developmental heats of 347 and Fe-20Cr-20Ni stainless steels processed as plate stock, and tested at 750°C and 100 MPa in air.
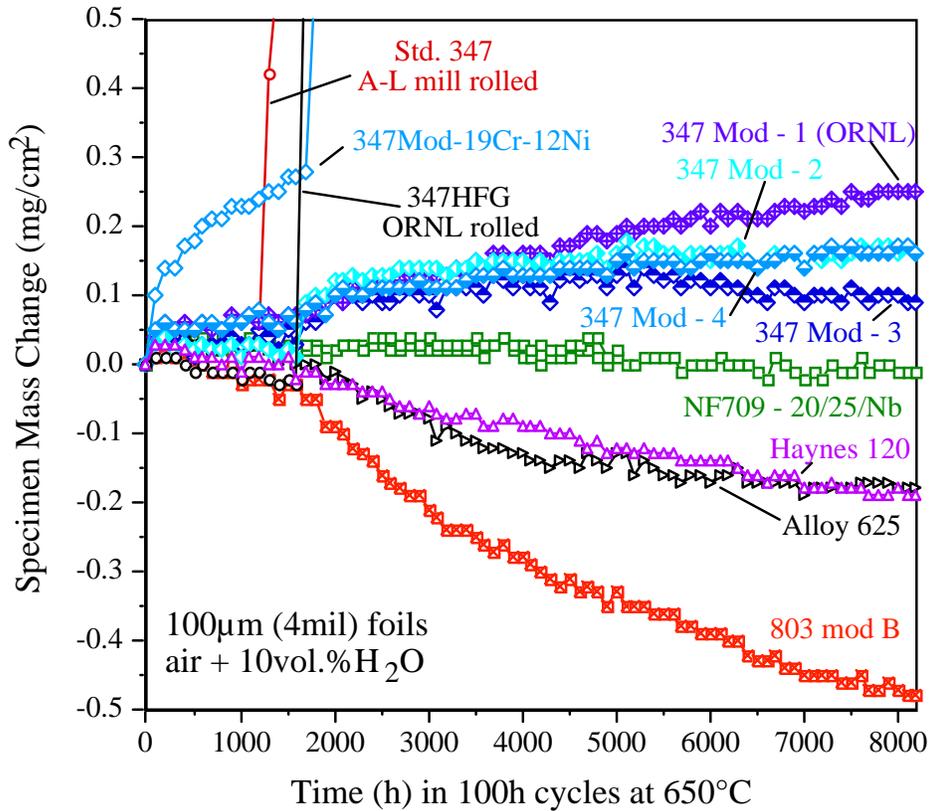
Figure 8 - Plots of oxidation weight change versus time for oxidation testing in air with 10% water vapor at 650°C. Specimens are cycled to room temperature every 100 h for microbalance measurements. Most materials are 0.1 mm foils processed at ORNL from commercial austenitic stainless steels and alloys, and Ni-based alloy 625, or ORNL developmental alloys. The standard, commercial 347 steels and one of the ORNL developmental 347 steel heats show the severe break-away oxidation attack after less than 2000 h at this relatively lower temperature, whereas the other ORNL modified 347 steels, and the higher Cr/Ni alloys (NF709, HR120, modified 803 and alloy 625) all show good resistance to such attack up to this point.
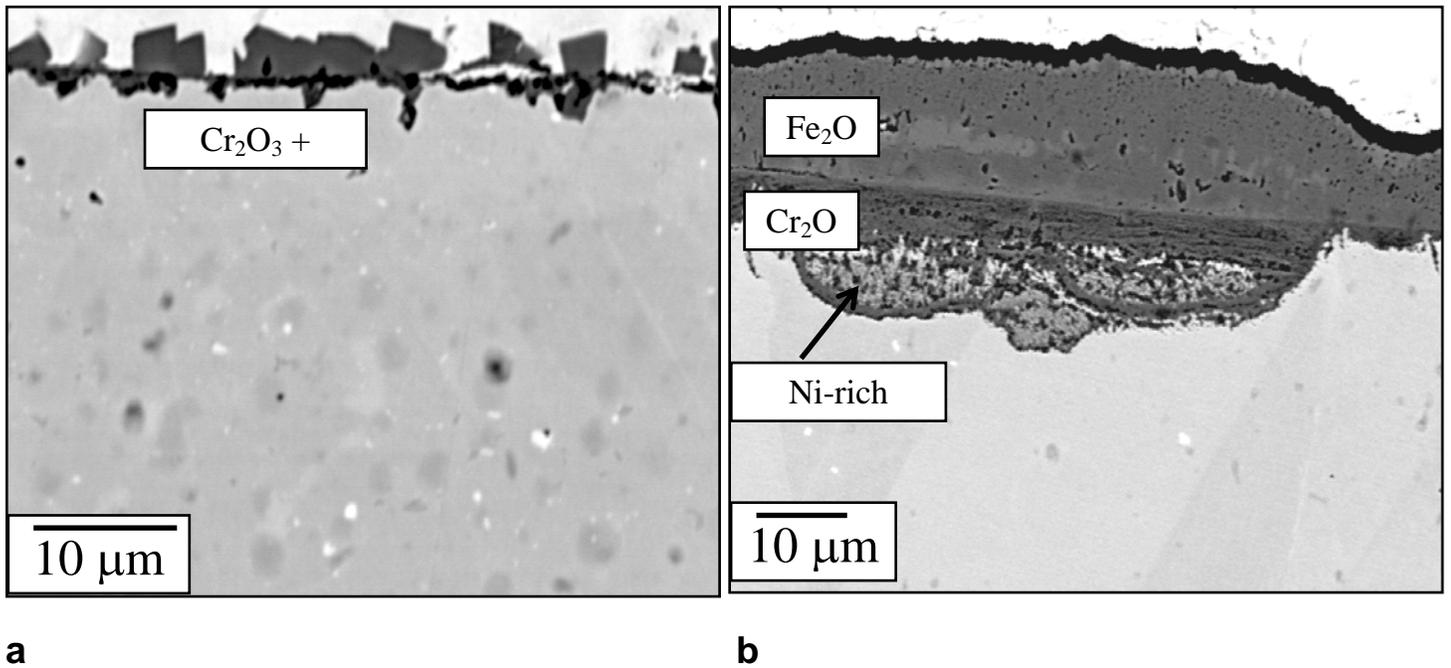
a　　　　　　　　　　　　　　　　　　**b**

Figure 9 – Backscattered SEM analysis of the oxidized surface of polished cross-sections of 347 stainless steel foils (0.1 mm) tested in air + 10% water vapor at 700°C for 1,000 h. a) ORNL developmental 347 stainless steel (mod.4), and b) standard, commercial 347 stainless steel. The Fe-rich surface oxide on top of the chromia oxide and corresponding subsurface attack are the microstructural signatures of moisture enhanced break-away oxidation attack in b). By contrast the modified 347 steel (mod.4) has a mixed oxide scale and is resistant to break-away oxidation at this point.
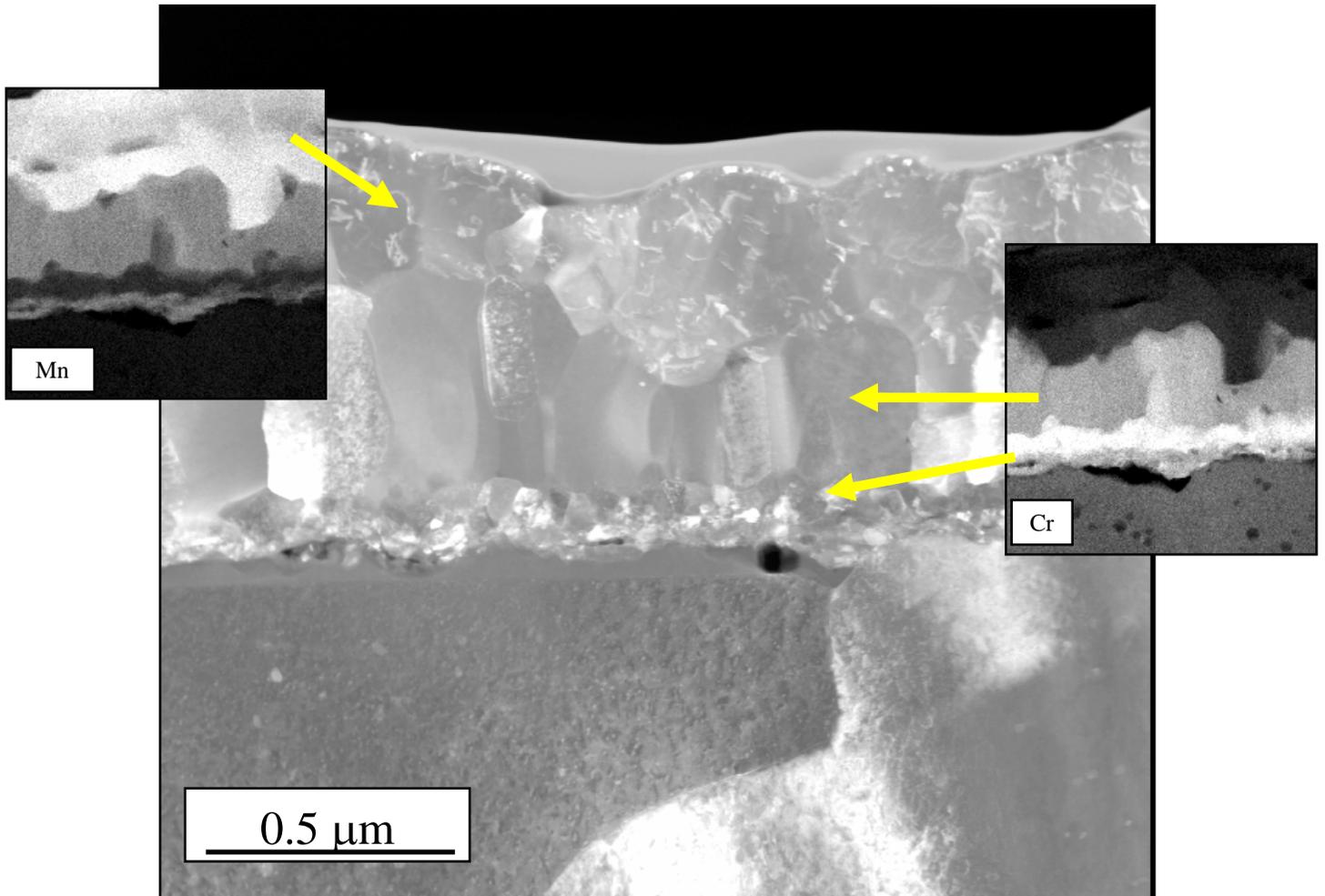
Figure 10 – Higher resolution microanalysis of the oxidized surface of the ORNL modified 347 (mod.4) stainless steel foil tested in air + 10% water vapor at 700°C for 1000 h (shown in Fig. 9) is obtained from analytical electron microscopy of a cross-section specimen electropolished so that the surface oxides and subsurface metal are electron transparent. The background picture is a transmission electron microscopy (TEM) image, while the two insets are high resolution X-ray maps using the characteristic Kα peak of the elements indicated. This analysis reveals that there is a Mn-rich oxide scale on top of the Cr-rich oxides that forms on the metal surface. This is likely an important feature in the stability of these oxide scales and the resistance of this Mn-modified 347 steel to moisture enhanced oxidation relative to standard 347 stainless steel.