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Improving High-Temperature Performance of Austenitic Stainless Steels for Advanced Microturbine Recuperators

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ABSTRACT

Compact recuperators/heat-exchangers are essential hardware for microturbines, and are also desirable for increased efficiency of small industrial gas turbines. Most commercial recuperators today are made from 347 stainless steel sheet or foil. Larger engine sizes, higher exhaust temperatures and alternate fuels will all require materials with better performance (strength, corrosion resistance) and reliability than typically found in 347 steel, especially as recuperator temperatures approach or exceed 700-750°C. To meet these needs, the Department of Energy (DOE) has sponsored programs at the Oak Ridge National Laboratory (ORNL) to generate data that enables selection of commercial sheet and foil materials, to analyze recuperator components, and to identify or develop more cost effective materials with improved performance and reliability. This paper summarizes data on the high-temperature creep behavior of both standard, commercial 347 steel sheet and foils typically used for commercial recuperators and as well as commercial HR 120 foil as a higher performance alternative. This paper also presents some of the initial data on standard 347 steel with modified commercial processing for improved creep resistance. Finally, ORNL efforts on lab-scale heats of 347 steels with modified compositions for improved corrosion and creep resistance are summarized.

INTRODUCTION

In contrast to larger industrial gas turbines, which operate at pressure ratios greater than 10:1, microturbines require recuperation of exhaust heat to achieve desired efficiencies of 30% or more [1-4]. Higher efficiencies mean higher recuperator temperatures, which challenge or exceed the performance of standard 347 stainless steel, which is used in commercial microturbine recuperators today. Since recuperators represent 25-30% of the overall microturbine first-cost, it is also very important to balance the need for higher performance and more durable materials with the need to make them as cost-effective as possible. There is a range of more heat-resistant and corrosion-resistant stainless alloys and superalloys commercially available, but they cost significantly more than 347 stainless steel.

The Department of Energy (DOE) has had an Advanced Microturbine Program [4] for several years, whose goal is to enable design and manufacture of advanced microturbines with efficiencies of 40% or more. Recently, interest in microturbines has expanded to include combined heat and power (CHP) and combined cycle (microturbines and fuel cells) applications, in addition to stand alone distributed power generation applications. Microturbines are attractive because they have very low

emissions and they are very fuel flexible (natural gas, flare gas, landfill and sewer gas, and various kinds of biofuels). Two of the main commercial microturbine vendors today in the U.S. are Capstone Turbines, Inc. and Ingersoll Rand Power Systems. Each manufactures its own recuperator, with Capstone producing an annular recuperator with primary surface (PS) welded air-cells [5], and Ingersoll-Rand making a stack recuperator with brazed plate and fin (BPF) air cells [6]. A typical BPF air cell from Ingersoll Rand is shown in Fig. 1. Both the PS and BPF recuperators are compact, counterflow, high efficiency heat exchangers, and they both have some common materials performance needs. To operate reliably at higher turbine exhaust temperatures, they both need materials with better high-temperature strength, creep and aging resistance, as well as better resistance to oxidation in environments containing significant levels of water vapor. However, each kind of recuperator has significantly different manufacturing and operating characteristics, so that there are different paths for upgrading and optimizing performance and reliability for each specific technology. Efforts to upgrade the performance of thin foil/sheet alloys also are directly relevant to heat-exhangers in other applications, including fuel reforming for fuel cells and high-temperature gas-cooled nuclear reactors.

The Oak Ridge National Laboratory (ORNL) has been doing materials research and development for improved high-temperature recuperator performance for several years [10-14]. Initial work focused on developing a systematic data base on lab-scale processed thin foils or sheet of commercial or developmental heat-resistant stainless alloys and superalloys, and included creep testing at 700-800°C and oxidation testing at 650-900°C. ORNL has also recently developed a recuperator test facility based on a modified Capstone 60 kW microturbine [15] for screening and evaluating a wide range of advanced materials.

The first section of this paper summarizes the initial effort to screen alloys for improvements in creep resistance at ORNL. The next section of this paper summarizes and highlights the most recent ORNL work on: a) measuring the creep resistance of standard, commercial 347 stainless steel foils and sheet currently used to manufacture recuperators, and of commercial HR 120 as a potential advanced recuperator alloy; b) efforts to modify the commercial processing of standard 347 steel to improve its creep resistance, and c) to develop new modified 347 stainless steels. The ultimate goal of this program is to facilitate manufacturing of air cells for different kinds of recuperators with upgraded performance and reliability, so that they can be evaluated in engine tests.

INITIAL CREEP TESTING OF HEAT-RESISTANT ALLOYS FOR SELECTION OF RECUPERATOR MATERIALS WITH IMPROVED PERFORMANCE

Commercial grades of the austenitic stainless steels and other alloys were obtained from 1.5 - 6.5 mm thick production-scale plate stock from a variety of commercial alloy producers. Standard T347 stainless steel was obtained from Allegheny-Ludlum; modified 803 developmental alloys, alloys 740 (formerly thermie-alloy) and 625 were obtained from Special Metals, Inc.; alloys HR120, HR214 and HR230 were provided by Haynes International, Inc.; and alloy 602CA was supplied by Krupp VDM. A piece of NF709 stainless steel boiler tubing, obtained from Nippon Steel Corp., was split and flattened for processing into foil. Alloy compositions (some supplied by vendors and other measured by Alstom Power Metallurgical Services Laboratory, Chattanooga, TN for ORNL) are given in Table 1. Plate and thicker sheets were hot-rolled, and the 0.1 mm thick foils were produced by a series of lab-scale cold-rolling and annealing steps at ORNL. Experimental details of processing, specimen preparation and creep-testing of these foils is given elsewhere [10,11].

There are several different measures of creep that are important to recuperator performance. These include rupture life, rupture ductility, and time to some level of strain that would significantly distort or affect the original component, which is probably less than 5-10% creep, depending on the specific recuperator type. Most commercial recuperators made from standard type 347 stainless steel operate at low stresses below 700°C, so that more aggressive creep testing at 100 MPa and 750°C was chosen as an accelerated screening condition for advanced alloys. Creep-rupture data for foil tested in air at that condition for standard 347 steel and various heat-resistant stainless alloys and Ni-based superalloys

are shown in Fig. 2. Alloys 625 and HR214 are very strong, and have much more creep-rupture resistance than 347 steel (rupture lives of 4000h for alloy 625 and 6000h for HR214, and both have much lower secondary creep-rates), so they are difficult to show on the same graph [10]. Alloy 740 (also formerly known as "thermie alloy") showed good creep-rupture resistance in the solution-annealed condition, and almost 20% rupture ductility. Alloys HR230, modified 803 and HR120 exhibited creep behavior between alloy 740 and 347 steel. Clearly, alloys 740, modified 803, HR120 and HR230 all have more creep resistance as foils than 347 stainless steel, whereas alloy 602CA has less. Some of these alloys would have a different ranking in relative strength as plate stock (particularly HR230 would be stronger), which justifies the need for data on sheet and foil performance for such applications. Similar testing of standard alloy 803 foil also shows that it is much less creep resistant than 347 steel [11]. These same alloys were also screened for the effects of aging for 2500h at 750°C on room temperature tensile ductility, which would be a factor for thermal fatigue due to cyclic operation. Here, both the modified 803 and HR120 alloy foils retained almost their original ductility after aging.

Alloy cost is an important factor to consider for advanced microturbine recuperators. Alloys 602CA, HR214, HR230, and 740 are all quite expensive, being up to 9 times the cost of 347 steel as plate, and possible more as sheet or foil [10]. Alloys 803 and HR120 are 3-3.5 times more expensive than 347 steel, and alloy 625 is about 3.5-4 times more [6,10]. Using either time to rupture or to 5% strain as a lifetime criteria, alloy 625 (3500h to 5% strain versus under 200h for 347 steel, for a performance/cost ratio of over 3) is a more cost effective alternative to 347 steel, but at an initially much higher initial cost. Alloy 625 also is much stronger at room temperature, so there may be manufacturing differences (ie. folding behavior) to consider relative to 347 steel foil. Using the same criteria of performance/cost ratio, HR120 and modified alloy 803 are similar to 347 steel, and HR214 is slightly better, and all of the other alloys are less cost effective than 347 steel. On the basis of creep resistance and cost, alloy HR120 appears to be the best commercially available higher performance alloy relative to 347 steel. Modified alloy 803 is still developmental [11,16].

COMMERCIAL MATERIALS TESTING AND EVALUATION FOR MANUFACTURING RECUPERATOR COMPONENTS WITH UPGRADED PERFORMANCE

Work was initiated at ORNL over a year ago on establishing a baseline measure for the creep resistance of the commercial 347 stainless steel foil and sheet stock used to manufacture recuperators. This was the first step in defining the benefit that use of the modified steels or advanced alloys would provide for upgrading the performance of commercial recuperator components. Foils and sheet of several different heats of standard 347 stainless steels that ranged from 0.076 to 0.254 mm in gage thickness were obtained from several different recuperator manufacturers and/or materials suppliers. Commercial 0.09 mm foil of HR120 was also obtained directly from Elgiloy Specialty Metals. Grain sizes ranged from as fine as 2-3 μ m to as coarse as 15 μ m or more in the various 347 steel foils and sheet specimens, but were coarser in the HR 120 alloy foil. Room temperature tensile properties were consistently similar among the various 347 steel sheet and foils, and the HR 120 alloy foil, with YS ranging from 310-340 MPa, and ductility from 46-65%.

Creep-rupture test data for these various foils and sheet specimens in air at 704°C and 152 MPa are shown in Fig. 3, and at 750°C and 100 MPa in Fig. 4. There is significant variability in the creep-rupture resistance of 347 steel sheet and foils, with rupture times ranging from 50 to 500 h, and rupture ductilities ranging from 3% to 27%. At 750°C and 100 MPa, rupture times ranged from 50 to 250 h, and rupture ductility ranged from 8 to 18%. There were some consistent, sensible metallurgical trends for the 347 materials, such as better creep resistance in thicker foils and/or with coarser grain size. However, there also are other factors influencing the creep resistance, because the thinnest gage foil was not the worst performer, nor is the specimen with the coarsest grain size the best. These data clearly indicated that there should be an opportunity to better control the processing and microstructure of standard 347

steel to consistently provide the best properties this alloy has to offer, and then use that to measure the benefit of higher performance alloys like HR 120.

Commercial HR120 foil consistently showed much better creep-resistance than standard, commercial 347 steel, lasting about twice as long without rupture as the best heat of 347 steel, and about 15 times longer than the worst 347 steel heat (Fig. 3). However, at a 5-10% creep strain limit, the improvement was slightly less, with the HR120 being 33-66% better than the best 347 steel. At 750°C, the HR120 lasted much longer than 347 steel (13 times longer than the best heat), which compares well with alloy 625 (3300 h and 4200 h, respectively), and had a rupture elongation of about 23% (Fig. 4). With the 5-10% creep strain limit, the HR120 was 4.5-6 times better than the best heat of 347 steel, but this was still a significantly better performance/cost ratio than was estimated based on the lab-scale processing data shown in Fig. 2. While the creep resistance of HR120 (creep rate and time to 5-10% strain) was lower than that of alloy 625 as foil products, these data for commercial HR120 alloy reinforce the previous conclusion that this alloy is a cost effective, higher performance alternative to standard 347 steel for foil applications. However, comparable creep data are needed on standard, commercial alloy 625 foil, and effects of better commercial processing on the creep resistance of 347 steel need to be determined to then enable a complete cost/benefit analysis to be performed for a specific recuperator. An example of such an analysis showing the factors affecting the choice of 347 steel versus alloy 625 for BPF recuperator performance is given by Kesseli et al. [6].

Analysis of current standard 347 steel recuperator air cells, in both the as manufactured and the engine-exposed conditions, was undertaken to provide base-line information from which to assess approaches for improvement. An example of a fresh braze joint from the middle of a BPF recuperator air cell component is shown in Fig. 1. This analysis shows a good, fresh braze joint between the 76 μ m 347 steel fin and the 0.254 mm 347 steel sheet plate. The Ni-Cr braze metal is forming nearly a continuous coating on the plate portion of the air cell. This is a different corrosion situation relative to the bare metal foils used to make most other kinds of recuperator, including the PS type. This effort now also includes real-time and accelerated PS air cell testing at the ORNL microturbine testing facility, based on a Capstone 60KW engine [15], to better screen relative alloy behavior, measure component or component-relevant properties, and enable testing and evaluating of changes made to upgrade recuperator materials performance.

Finally, a collaborative project was initiated late last year between ORNL and Allegheny-Ludlum Technical Center (ALTC) to provide commercial coils of standard 347 stainless steel foil, processed to have consistently better creep resistance. Ingersoll-Rand Energy Systems has provided specifications for and will take delivery of commercial quantities of the 347 foils and sheets used for manufacturing of their BPF recuperator air cells. Nominal amounts of 0.1 and 0.127 mm foil products also are being made by ORNL and ALTC to extend the study to a wide range of products. Commercial processing parameters have been adjusted to, at a minimum, coarsen the grain size to improve the creep resistance of standard composition T347 steel. The results comparing normal and modified processing for 75-80 um foils and 0.254 mm sheet of the same commercial heat of T347 steel after creep testing at 704°C and 152 MPa in air are shown in Fig. 5. Microstructural analysis of both T347 and T347CR as-processed 0.254 mm sheets to determine grain size (metallography) and intragranular NbC differences (transmission electron microscopy (TEM)) are shown in Fig. 6. The creep rupture life of the foil was improved 100% and sheet was improved by 34% by the modified processing and changes in microstructure. The improvements are greater considering a 5% creep strain limit, with 133% for the foil and 90% for sheet. The 0.254 mm sheet clearly shows that the largest change in microstructure due to the change in processing was the elimination of nearly all of the smallest size grains, most likely due to coalescence. Comparing the commercial HR120 foil (Fig. 3) to the T347CR (Fig. 5) for creep at 704°C, the time to 5% creep strain is now similar, although the former still has a little more than twice the rupture life. These early results clearly indicate that a considerable improvement in the creep resistance of standard composition 347 steel foils and sheet can be made through careful selection of processing conditions.

Clearly an immediate and cost effective improvement in recuperator performance could be made simply from optimizing the performance of standard 347 steel. Work continues to creep test these foils

and sheet at 750°C and 100 MPa, and to include foils with various thicknesses in this comparison. TEM microstructural analysis also will be completed on the creep tested specimens of the T347CR to determine and understand the role of NbC precipitation in the improvements in creep-rupture resistance.

DEVELOPMENT OF MODIFIED 347 STAINLESS STEELS AND ALLOYS FOR HIGHER TEMPERATURE CAPABILITY

A unique and important aspect of the ORNL work for the last several years has been lab-scale alloy development to modify the composition of 347 stainless steel to significantly improve both the creep-resistance and corrosion-resistance, if possible [10,11]. While one primary driver for this effort has been the expressed desire of microturbine recuperator makers to provide near-term improvements in performance and durability at the lowest possible cost, another added incentive and opportunity is the recent success achieved by using processing to boost the creep resistance of standard composition 347 steel described above. Several 15 lb heats of 347 stainless steels with modified compositions were melted at ORNL, hot-rolled into plate, then cold-rolled into 0.1 mm thick foils, and finally annealed. The composition ranges of three of the modified 347 steels for the elements common to standard 347 steel are summarized in Table 1, but the several alloying additions that make them different are not disclosed at These modifications and additions were specifically designed to produce "engineered this time. microstructures," for better aging- and creep-resistance at 700-800°C compared to standard 347 steel, at little or no increase in alloy cost. Data on aging resistance of two of these modified 347 steels (alloys 3 and 4) and oxidation data in 10% water vapor at 800°C have been presented recently [10,11], and creeprupture data for the best alloy (alloy 4) at 750°C and 100 MPa are shown in Fig.7. For comparable labscale foil processing, the ORNL mod 347-4 showed over twice the rupture life and 7 times longer time to 5% strain than standard 347 steel. The creep rate of the modified 347-4 compared well with that of alloy 625 until it ruptured. TEM analysis showed that abundant, fine intragranular precipitation, including NbC, and resistance to sigma phase formation, are the microstructural differences that cause the improved creep resistance of the modified 347-4 steel, as shown in Fig. 8.

The various modified 347 steels also showed improved corrosion resistance compared to standard 347 steel. Accelerated oxidation testing for about 1000 h at 800°C in 10% water vapor, to simulate the gas turbine exhaust gas. The improved corrosion resistance of the mod. 347-4 steel at 800°C was found to be directly related to a delay in the onset of break-away oxidation and the formation of non-protective surface mixed Fe-Cr oxides and the associated subsurface metal degradation [7-9,11,14].

Corrosion resistance and the exacerbating effects of moisture become dominant limiting factors for 347 steel at test temperatures of 650 to 700°C, which is more relevant to current microturbine recuperator operating conditions [11,12,14]. Oxidation test data at 650°C in 10% water vapor for up to 6000 h are given in Fig. 9. The new modified 347 steels all show much better resistance to oxidationin water vapor at 650°C than standard 347 steel. These limited, initial test data also clearly show that the new modified 347 steels have oxidation resistance that is comparable to the excellent behavior normally found in alloys 625, modified 803, HR120, and NF709, all of which have substantially more Cr and Ni. While these preliminary results do not mean that the modified 347 steels will not eventually exhibit the breakaway oxidation in water vapor, the delay in such severe oxidation attack does provide a substantial added benefit of these new alloys for near-term recuperator applications, particularly when combined with their creep resistance. The next step will be to make 1 or 2 larger commercial heats of the best modified 347 steels, so that high quality commercial foil can be made for recuperator component manufacturing trials.

Detailed microstructural analysis of a cross-section of standard 347 foil coupon tested at 700°C and 10% water vapor to oxidation behavior near the surface is also shown in Fig. 10. The lower magnification back-scattered SEM image shows directly the heavy surface deposits of iron-rich oxide and the corresponding deep subsurface oxide penetration that significantly reduces the remaining thickness of unaffected metal that are typical of 347 steel suffering breakaway oxidation attack (Fig. 10a). The higher

magnification SEM image in Fig. 10b, made by mapping with the characteristic Cr K α x-ray peak in a region with less surface attack, clearly shows the thin chromia layer that remains underneath the Fe-rich oxide deposit, and narrow Cr-depleted grain boundaries just below the chromia scale. This characteristic subsurface structure is caused by the combination of diffusion along the grain boundaries and Cr depletion due to formation of the chromia scale at the surface. The Cr-map image also shows small particles of Cr-rich sigma phase forming along grain boundaries deeper in the foil with much less Cr depletion. Consistently, the subsurface layer with the most Cr depletion along the grain boundaries also shows no formation of Cr-rich sigma phase particles. This characteristic subsurface structure develops rapidly in both recuperator components and lab-test foil coupons, and generally preceeds the formation of the thick Fe-rich surface oxide deposits or break away oxidation. Such microstructural behavior is important in understanding how the advanced stainless steels and alloys resist such attack. Similar microstructural characterization of the modified 347 steels and foils of the advanced alloys is currently being done.

CONCLUSIONS

A group of cost effective alloys with more aging, creep and oxidation/corrosion resistance than standard 347 austenitic stainless steel has been identified for advanced microturbine recuperator applications. Alloy 625 is a very high performance alternative to 347 stainless steel for recuperator applications that may be useful at up to 750°C. However, alloy 625 also has a substantially higher first cost. HR120 is a commercially available alloy with good creep-resistance at 700-750°C that is a more cost effective performance upgrade relative to standard, commercial 347 steel foil. Both HR120 and 625 alloys have much better oxidation resistance in water vapor at 700-800°C than 347 steel.

Initial creep testing shows that adjustments to commercial sheet and foil processing to tailor the microstructure of standard 347 steel significantly improves the creep resistance at 750°C and 100 MPa. Such improvements should provide immediate benefits for recuperators up to or slightly above 700°C. Preliminary lab-scale alloy development data indicate that substantial improvements in both creep and oxidation/corrosion resistance are possible in modified 347 steels for use at 700-750°C, and which should have about the same cost as standard 347 steel. Development of such modified 347 steels and related austenitic stainless alloys with a better combination of creep-resistance and oxidation resistance should lead to commercial scale-up and foil processing trials. These will provide near-term cost effective recuperator performance upgrades that are not as costly as using HR120 and 625 alloys.

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Alloy/vendor	Fe	Cr	Ni	Мо	Nb	С	Si	Ti	Al	Others
347 steel (Allegheny-Ludlum)	68.7	18.3	11.2	0.3	0.64	0.03	0.6	0.001	0.003	0.2 Co
modified 347 steels (ORNL, mod 2-4)	58	18-19	12.5	0.25	0.4	0.03	0.4	-	-	n.a.
NF 709 (Nippon Steel)	51	20.5	25	1.5	0.26	0.067	0.4	-	-	0.16 N
modified 803 (Special Metals, developmen	40 tal)	25	35	n.a.	n.a.	0.05	n.a.	n.a.	n.a.	n.a.
alloy 740 ("Thermie") (Special Metals)	2.0	24	48	0.5	2.0	0.1	0.5	2.0	0.8	20 Co
alloy 120 (Haynes International)	33	25	32.3	2.5 max (0.7	0.05	0.6	0.1	0.1	3 Co max 3 W max 0.2 N
alloy 230 (Haynes International)	3 max	22	52.7	2	-	0.1	0.4	-	0.3	5 Co max 14 W +trace La
alloy 214 (Haynes International)	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	
alloy 602CA (Krupp VDM)	9.5	25	63	-	-	0.18	-	0.15	2.2	0.06 Zr, 0.08 Y

Table 1 – Compositions (v	vt.%) of Heat-Resistant	Austenitic Stainless	Alloys Processed in	nto Foils at
ORNL			-	

n.a. – not available



Figure 1 – An air cell from the recuperator of an Ingersoll-Rand 70 kW PowerWorks microturbine showing the folded fins brazed onto the plate at lower (upper) and higher (lower left) magnification, and SEM of a typical Nibraze alloy joint cross-section (lower right). The fin and the plate are made from 347 stainless steel.



Figure 2 – Plots of creep strain versus time for creep-rupture testing of a range of commercial heat-resistant alloys in air at 750° C and 100 MPa. The alloy designated "Thermie" has recently been named alloy 740 by Special Metals. All were supplied as thicker plate and processed into lab-scale 0.1 mm thick foils at ORNL.



Figure 3 – Plots of creep strain versus time for creep-rupture testing at 704°C and 152 MPa. All specimens were made from standard, commercial 347 foil and sheet stock supplied by recuperator manufacturers or materials suppliers. Commercial foil of HR 120 was supplied by Elgiloy.



Figure 4 – Plots of creep strain versus time for creep-rupture testing at 750° C and 100 MPa. The 347 steel specimens were from commercial recuperator foil or sheet stock, the commercial foil of HR 120 was supplied by Elgiloy, and foil of the commercial alloy 625 was made into lab-scale foil at ORNL.



Figure 5 - Plots of creep strain versus time for creep-rupture testing in air at 750°C and 100 MPa. Standard, commercial foil and sheet of 347 steel are compared to similar standard 347 sheet and foil with modified processing conditions designed to change the microstructure to enhance creep resistance (T347CR).



Figure 6 – Microstructure analysis comparing 10 mil sheet comparing T347 (a, c) with standard processing and T347CR (b, d) with modified processing. Metallography is shown in a) and b), while TEM is shown in c) and d).



Figure 7 - Plots of creep strain versus time for creep-rupture testing of a commercial standard 347 foil #1, and ORNL lab-scale processing of standard 347, standard 625 and an ORNL lab-heat of a modified 347 stainless steel (347-4). All are 0.1 mm thick foils creep tested in air at 750° C and 100 MPa.



Figure 8 – TEM analysis of microstructures from the gage portions of the creep specimens tested at 750° C at 100 MPa in air, and whose creep curves are shown in Fig. 7. Both are 0.1 mm thick foils processed on a lab-scale at ORNL of A) standard 347 from commercial plate and B) modified 347 stainless steel (347-4) from an ORNL lab-scale heat. The obvious difference in intragranular precipitate dispersions is directly responsible for the differences in creep resistance.



Figure 9 – A plot of mass change as a function of exposure time for specimens tested in air with 10% water vapor at 650° C, with cycling to room temperature every 100h to weigh specimens (upper). All specimens are 0.1 mm thick foils of several commercial heats of standard 347 steel, commercial heats of alloys NF709, 625 and HR120, and labscale heats of modified 347 steels and modified alloy 803, processed on a lab-scale at ORNL.



Figure 10 - The microstructure of a cross-section of standard 347 steel (347 A-L) tested in 10% water vapor at 700°C for 1000h is analyzed using backscattered SEM (lower left) and higher magnification X-ray mapping of Cr near the surface. The heavy Fe-rich surface scale and sub-surface attack is typical of break-away oxidation attack in the presence of water vapor.