Selecting and Developing Advanced Alloys for Creep-Resistance for Microturbine Recuperator Applications

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ABSTRACT

Recuperators are considered essential hardware to achieve the efficiencies desired for advanced microturbines. Compact recuperator technologies, including primary surface, plate and fin, and spiral, all require thin section materials that have high-temperature strength and corrosion resistance up to 750°C or above, and yet remain as low-cost as possible. The effects of processing and microstructure on creep-rupture resistance at 750°C and 100 MPa were determined for a range of austenitic stainless alloys made into 0.1 mm foils. Two groups of alloys were identified with regard to improved creep-resistance relative to type 347 stainless steel. Alloys with better creep-rupture resistance included alloys 120, 230, modified 803 and thermie-alloy, while alloy 214 and 625 exhibited much better creep strength. Alloys 120 and modified 803 appeared to have the most cost-effective improvements in creep-strength relative to type 347 stainless steel, and should be attractive for advanced microturbine recuperator applications.

INTRODUCTION

Microturbines are a new and increasingly exciting subset of combustion gas turbines being used and improved for stationary power generation. Microturbines have generally evolved from automotive or aerospace small turbine applications, or from efforts to make industrial turbines smaller, and tend to fall in the 5 to 500 kW size range [1]. They are an important part of the evolving distributed power generation picture, both for stand-alone generation and for combined cycle applications with fuel cells [2].

Microturbines have several design features that are unique relative to larger industrial engines. Microturbines operate at higher speeds and lower pressure ratios than larger gas turbines, and they need recuperation of exhaust heat to achieve desired efficiencies [1,2]. Low-cost materials are also a must for mass producing microturbines. Compact recuperators are heat-exchangers that boost the thermal efficiency of current microturbines to about 30% (about 20% without recuperation), and are essential for advanced microturbines to achieve the desired efficiencies of up to 40%. Recuperators also significantly muffle the noise from turbines [2-4], which is important in many potential applications. Recuperators represent 25-30% of the overall microturbine cost, so it is extremely important to balance the need for high performance and durable materials with the need to make them as cost-effective as possible.

There are several different kinds of compact metallic recuperator technologies available for microturbines, including primary surface, plate and fin, and spiral recuperators, each with a variety of final configurations designed for specific engine applications [1-6]. While some envision ceramic recuperators in the future [1], most current compact recuperators are manufactured from austenitic stainless steels like type 347 or from heat-resistant Ni-based alloys like 625 [1,4]. Last year, the Department of Energy initiated a new Advanced Microturbine Program [7] and awarded contracts to turbine manufacturers (Capstone, Honeywell, General Electric, United Technologies Research Center and Ingersoll-Rand) to design and build microturbines with efficiencies of 40% or more. The only way to achieve that efficiency is higher operating temperatures. Such advanced microturbines will push the metallic recuperator maximum temperatures to 750°C or higher and demand service lifetimes of 45,000 h or more [7]. Although critical or life-limiting properties vary for each of the different compact recuperator technologies, they all require thin-section alloys with good resistance to oxidation in moist air or exhaust, and good resistance to creep, fatigue, or fracture at 750°C or above. They also need sufficient ductility at room-temperature for various component manufacturing processes and probably need to be as close to the cost of type 347 stainless steel as possible. There is a range of commercial heat-resistant and corrosion-resistant alloys available that fall between type 347 stainless steel and alloy 625, and there are comprehensive data bases, selection rules and design guidelines for such high-temperature alloys for thick-section pressure-vessels and piping applications [8-10]. However, there are few such data on most of these alloys processed into thin-sections or foils specifically for use in selecting materials for or designing recuperators. Processing variations can dramatically affect and improve the creep-resistance of type 347 stainless steel foils at 700°C [11]. Therefore, the purpose of this work is to provide a preliminary but systematic data base on a range of heat- and corrosion-resistant alloys between type 347 stainless steel and alloy 625 processed appropriately into foils and creep-tested at 750°C and above. These data should be useful to aid materials selection for microturbine recuperator applications. This work is also intended to provide a sound physical metallurgical basis (processing, properties, microstructure correlations) for further modifying or developing alloys with improved performance that are most cost-effective relative to type 347 stainless steel for advanced microturbine recuperator applications. This work is a portion of the new DOE Advanced Microturbines Program [7].

EXPERIMENTAL

All of the austenitic stainless steels and alloys were commercial grades obtained from production-scale plate stock that was 1.5 – 6.5 mm thick. Type 347 stainless steel was obtained from Allegheny-Ludlum, modified 803 developmental alloys, thermie-alloy and alloy 625 were obtained from Special Metals, Inc., and alloys 120, 214 and 230 were provided by Haynes International, Inc. Alloy compositions are given in Table 1.

Pieces of each alloy were processed into 0.1 mm thick foils using laboratory-scale processing equipment at ORNL. The general processing steps were similar for most of the alloys, but specific processing parameters, particularly the final steps, were tailored for each individual alloy, based on processing information for thicker products given by the materials producers, and on experience in alloy processing at ORNL. Generally, the goal was to produce foils with about 5-10 grains across the thickness. Alloys were reduced to 1.3 mm thickness by hot-rolling at 1150°C or above, and then further reduced by a series of cold-rolling and solution-annealing steps into foils. Annealing times and temperatures varied from several minutes to over 30 minutes at 1050 to 1200°C depending on the alloy, with final annealing temperatures being slightly lower and times much shorter to control the final grain size. Anneals of thicker materials were performed in an argon muffle in a large box (air) furnace, whereas the final anneals of thin foils were done in a special radiant-heating furnace (high-intensity tungsten-halogen lamps for very rapid heating and cooling), with precise measurement and control of time and temperature and an argon-4%hydrogen atmosphere to produce a bright finish.

Creep specimens were laser-cut from as-processed foil with 25.4 mm long and 6.4 mm wide gages. The specimens were creep-tested in special pin-hold grips designed for foils, in dead-load machines with LVDT strain sensors and computerized data acquisition systems. All specimens were evaluated by creep-rupture testing at 750°C and 100MPa, with a few tests also being done at 800°C and lower stress. Several of the alloys were tested to evaluate differences in processing conditions.

Optical metallography was performed on all the as-processed alloys to determine the final grain size and observe the amount of undissolved precipitates or other phases. More detailed analytical electron microscopy (AEM) was done on a few of the alloys to observe and identify finer precipitates in the matrix and along grain boundaries, using a Philips CM30 (300KV, LaB_6 gun), a Philips CM200 (200KV, field emission gun) or a Philips Tecnai 20 (200KV, LaB_6 gun).

RESULTS

Figure 1 shows the typical range of grain sizes obtained for the more heat-resistant and corrosion-resistant alloys relative to type 347 stainless steel. Both the type 347 stainless steel and alloy 214 had coarser grain sizes than desired (>20 μm), while the grain size in the thermie alloy was finer and similar to the other alloys processed at ORNL. Processing of alloys 214 and 625 was varied to refine the grain size, but only the alloy 625 had a much finer grain size (>5 μm).

The plots of creep strain versus time of the various alloys after creep-rupture testing at 750°C and 100 MPa are shown in Figures 2 and 3. The creep response can be separated into two groups, with the thermie alloy being the dividing line common to both groups. The first group is the alloys that are somewhat better than type 347 stainless steel, with alloy 120 and modified alloy 803 lasting 2-3 times longer and also having more than double the rupture elongation. Alloy 230 is a little weaker than the modified 803 (Fig. 2), but has about 5% more rupture elongation. Clearly, thermie-alloy has much more creep resistance than this first group of alloy, lasting 2000 h instead of 600-750 h, and still having close to 20% rupture elongation. The second group includes alloys 214 and 625, which are considerably stronger and last much longer than thermie-alloy (Fig. 3). Alloy 214 is the best at these conditions, lasting almost 6000 h and still having close to 10% rupture elongation.

Two processing variations were included for alloy 625, one with a much finer grain size and the second with a finer grain size and a small amount of additional cold tensile prestrain (2.5%) (Fig. 4). The fine-grained foil is significantly less creep-resistant relative to the coarser-grain foil, which is expected, while the small amount of added prestrain actually improves the creep-resistance slightly. Two processing variations were also included for alloy 214, with the shorter anneal producing a slightly finer grain size than the longer anneal (Fig. 5). Both show good creep resistance at 800°C and 80 MPa, with the material having slightly coarser grains also being slightly better.

AEM analysis was performed on the 347 stainless steel, and alloys 625 and 214, with the latter two being shown in Figure 6. The stabilized 347 steel has only some coarser NbC particles in austenite grains that are otherwise free of any other types of carbides. The alloy 625 has some patches of very fine particles and sparce clusters of much coarser particles in otherwise austenite grains. High special resolution X-ray energy dispersive spectroscopy (XEDS) microcompositional analysis revealed that the coarse particles are all Ti- and Nb-rich MC carbides (about 80% Ti, 20% Nb), while the fine precipitates are Nb-rich eta silicides (roughly equal parts of Nb, Cr, Si and Ni). AEM analysis of alloy 214 shows that there is a very fine and uniform dispersion of coherent Ni_3Al (γ') precipitates in the austenite grains and along grain boundaries, clearly identified by electron diffraction. AEM analysis of all the other as-processed alloys is in progress and some of the creep-tested specimens will also be analyzed to determine the nature of their creep-resistance. The fine γ' precipitation prior to creep in alloy 214 is clearly a difference relative to the other primarily solid-solution alloys, and is consistent with the robust creep-resistance this alloy exhibits. Knowing and understanding the high-temperature strengthening mechanisms in each of these different alloys provides important feedback as to whether or not further processing modifications or alloy development are likely to improve the observed creep-resistance.

DISCUSSION

Creep-rupture testing provides just one measure of performance for ranking or selecting materials at elevated temperatures, but above 600-650^{o}C where creep can limit the lifetime of Fe-Cr-Ni stainless steels and alloys, it can be a better indicator than tensile properties alone. Ultimate tensile strength and total elongation of the various alloys considered in this work are given in Table 2, and are taken from either alloy data sheets available from the various materials producers (Allegheny Ludlum, Special Metals or Haynes International) or the literature [12]. For thin-section compact recuperators for microturbines, both creep and oxidation resistance, particularly with water vapor effects included, are important life-determining parameters that must be considered for materials selection [4,13-15]. However, for the different kinds of compact recuperators, other properties, including cyclic and thermal fatigue, and thermal expansion are also important, and relative cost is an essential consideration. With regard to oxidation resistance, studies in 4-15% water vapor at 700-800^{o}C indicate that above 700^{o}C, stainless steels and alloys with over 20 wt.% Cr will perform better than stainless steels with lower Cr [14,15], and that alloys like 625 (22 wt. Cr) and 214 (16 wt.% Cr + 4.5 % Al) show very good behavior under such conditions [16]. With the exception of alloy 214 which contains both Cr and Al, all of the heat-resistant alloys included in this study have 22-25 wt.% Cr and Ni levels of 35% or more (Table 1).

Ranking the alloys according to creep-rupture resistance at 750^{o}C as foils is generally consistent with the relative differences in their ultimate tensile strengths (UTS) as thicker wrought products, but there are several important exceptions. While thermie-alloy has the highest UTS at 750^{o}C, its creep-rupture resistance is significantly lower that alloys 625 and 214, with 214 being clearly the best of the alloys tested. Alloy 230 has UTS similar to alloy 625, but the creep-resistance is only somewhat better than type 347 stainless steel, and a little less than the creep resistance of the modified alloy 803, which has about half the UTS of alloy 230. Clearly, alloy 230 ranks lower in relative creep resistance as a foil product than alloy 120 or modified alloy 803. Both total tensile elongation and creep-rupture elongation at 750^{o}C are also important factors to consider in trying to assess reliability and durability during long-term service, particular regarding resistance to cracking in an aggressive, corrosive environment. In terms of tensile elongation for thick-section products, the modified alloy 803 and alloy 625 have the highest ductility, which gives alloy 625 the highest combination of UTS and total elongation of the alloys considered. The other alloys all show >40% elongation, with thermie alloy having 30% and alloy 214 having only 15%. As finer grained foil products, type 347 steel and alloys 214 and 625 have creep-rupture ductilities of about 10% or less. Alloy 214 maintains its ductility after creep, despite being a relatively coarser grained foil. Alloy 625 shows much lower creep-rupture ductility relative to its total tensile elongation, and even very fine grained foil has about the same rupture ductility. The other austenitic alloys all show > 20% creep-rupture ductility (about twice that of type 347 steel), with alloy 230 having the best (about 25%).

When considering rough relative cost estimates of these stainless alloys compared to type 347 stainless steel, the modified 803 and alloy 120 appear to be about 3 times more expensive than type 347 [13], which is significantly less than alloy 625 which is about 5 times more expensive. Since alloy 230 and thermie-alloy would fall closer in cost to alloy 625 (based mainly on alloy composition without regard to processing), and alloy 214 is even more expensive, the most cost-effective alloys with improved performance for microturbine recuperator applications in the temperature range of 700-750^{o}C appear to be alloy 120 and the new modified alloy 803. Since both alloys have about 25% Cr supported by higher alloy Ni contents, they should also have much better oxidation/corrosion resistance than type 347 stainless steel, even in a moist exhaust environment.

Clearly these data are very preliminary, and there is a need for long creep-tests at lower stresses as well as appropriate corrosion testing in water vapor, but both of these alloys warrant further investigation, particularly with regard to specific recuperator component fabrication issues such as formability, welding or brazing. In terms of even higher metallic foil performance, both alloys 625 and 214 should be able to withstand temperatures of 800^{o}C or above, but the same component fabrication issues must also be addressed.

Finally, another consideration for selection of these alloys in various compact recuperator applications is thermal expansion [4,13]. Type 347 stainless steel has relatively higher thermal expansion than the other austenitic alloys considered here, with the relative expansion decreasing with increasing Ni content. Alloy 625 has 20-25% less expansion than type 347 stainless steel in the temperature range of 600-800^{o}C, with alloy 120 and modified alloy 803 falling about half way in between. Although the specific effects of thermal expansion are different in each of the various microturbine recuperator technologies, there is a definite benefit to lower thermal expansion, which provides an added benefit when considering replacement of type 347 stainless steel with alloy 120 or modified alloy 803.

Microturbine recuperator design and performance should be enhanced by continued development of a systematic data base of alloy properties derived for appropriately processed thin-section or foil, and including a range of stainless alloys and superalloys. Moreover, metallurgical insight into the microstructure/processing relationships and the effects of such microstructures on creep and aging mechanisms of thin section alloys should at least allow performance optimization for given alloys like alloy 120 or modified 803. Such data may also enable significant modifications to develop new, more cost-effective alloys in between these standard alloys and type 347 stainless steel. Such data will also be applicable to the other thin section hardware that supports the compact recuperator cores, including containment, ducting and flexible connectors.

CONCLUSIONS

A group of heat-resistant and oxidation/corrosion resistant austenitic stainless alloys have been processed into 1.3 mm foils and creep-rupture tested at 750°C and 100 MPa. Alloys 230, 120 and modified 803 lasted several times longer than type 347 stainless steel, while thermie-alloy was almost ten times better. Alloys 625 and 214 showed much better creep-rupture resistance than thermie-alloy, with alloy 214 showing the best behavior observed for this entire group. Thermie-alloy, and alloys 625 and 214 probably have the potential for use at low stresses at 800°C and above. These alloys are also sensitive to variations in processing parameters. Because alloys 214 and 625 are considerably more expensive than type 347 steel, alloy 120 and modified alloy 803 may be the most cost-effective alternatives to type 347 steel for microturbine recuperator applications, particularly if they demonstrate good resistance to oxidation in moist exhaust gas. Minor alloying or processing modifications may also further improve the creep resistance of both of these alloys

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

Alloy/vendor	Fe	Cr	Ni	Mo	Nb	C	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 803 (Special Metals, developmental)	40	25	35	n.a.	n.a.	0.05	n.a.	n.a.	n.a.	n.a.
thermie-alloy (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	

n.a. – not available

Table 2 – Typical Tensile Properties of Heat-Resistant Austenitic Stainless Alloys Wrought Plate or Tube at 750°C

Alloy	Ultimate Tensile Strength (MPa)	Total Elongation (%)
347 stainless steel	240	45
modified alloy 803	310	63
alloy 120	485	45
alloy 230	590	45
thermie-alloy	795	30
alloy 214	690	15
alloy 625	620	70

(data from the literature or data sheet from materials suppliers)

Figure 1 – Optical metallography of polished and etched specimens of as-processed 0.1 mm thick foils to show grain sizes of a) type 347 stainless steel, b) thermie-alloy, and c) alloy 214

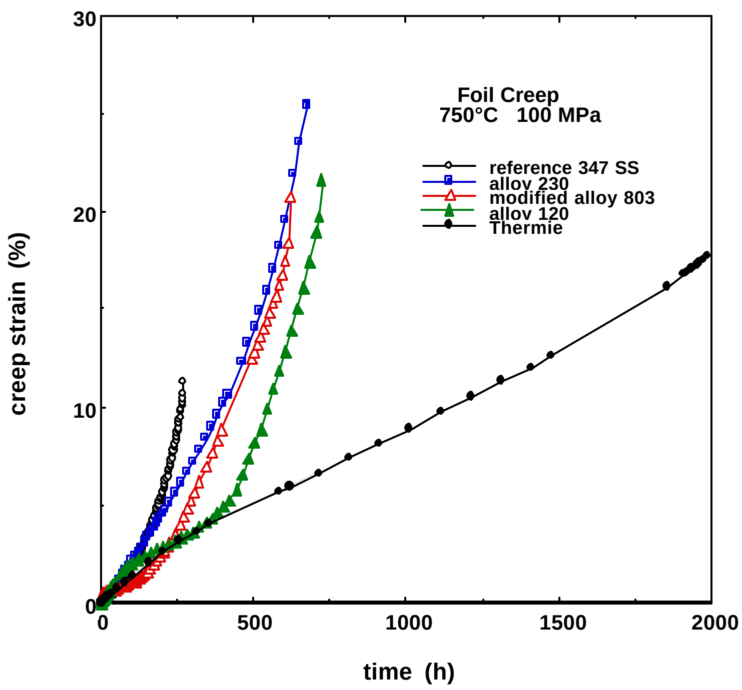

Figure 2 – Plots of creep strain versus time for creep-rupture testing of foils ranging from type 347 stainless steel to thermie-alloy at 750^{o}C and 100 MPa.

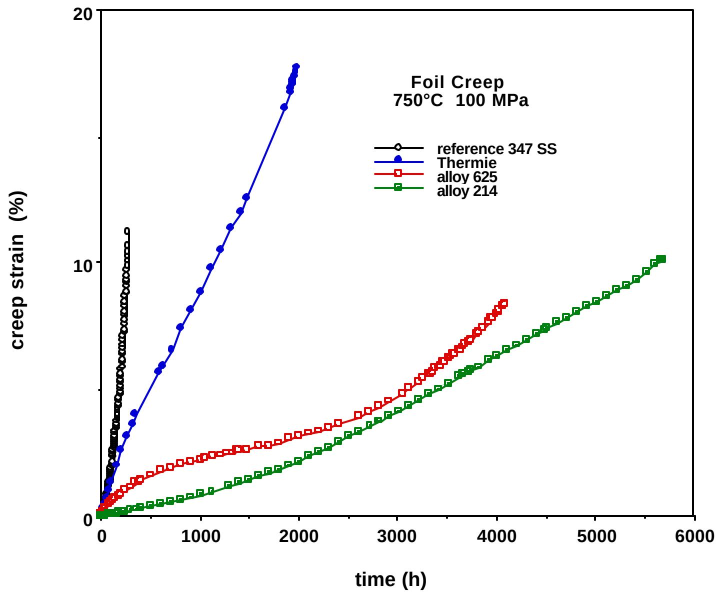

Figure 3 – Plots of creep strain versus time for creep-rupture testing of foils ranging from type 347 stainless steel to alloys 625 and 214 at 750°C and 100 MPa.

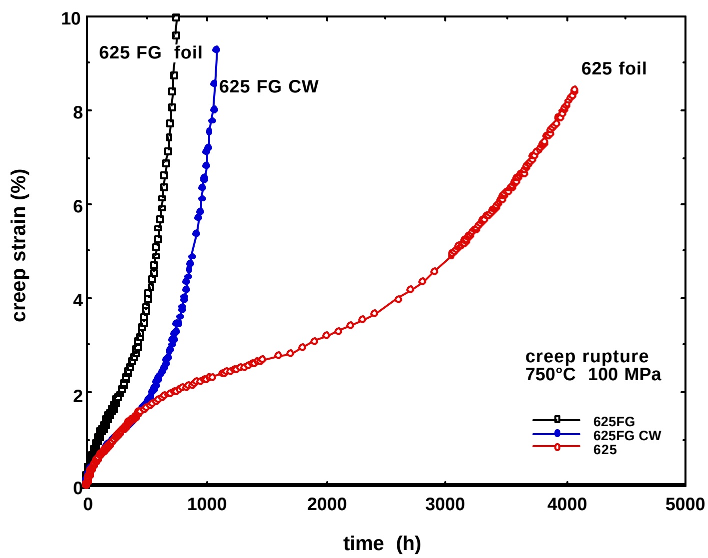

Figure 4 – Plots of creep strain versus time for creep-rupture testing at 750°C and 100 MPa of foils of alloy 625 processed at different conditions (FG = fine grained) or with 2.5% cold prestrain.

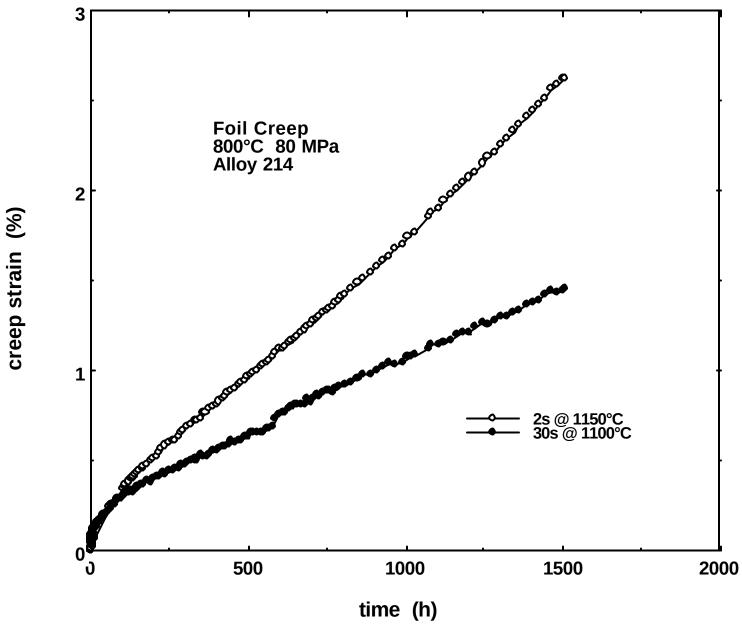

Figure 5 - Plots of creep strain versus time for creep-rupture testing at 800^{o}C and 80 MPa of foils of alloy 214 processed at different conditions that slightly vary final grain size, with 2s at 1150^{o}C being finer.

Figure 6 – TEM images showing the microstructures within grains and along grain boundaries for as-processed foils of a) alloy 214 with a final solution anneal (SA) of 30s at 1100^{o}C, and b) alloy 625 (FG) with a final recrystallization anneal of 30s at 900^{o}C. The superimposed diffraction pattern shows the characteristic extra spots from the γ' (Ni_3Al) coherent precipitates shown as black spots in the image. The alloy 625 had coarser precipitate particles of Ti- and Nb-rich MC carbides and finer η phase silicides.