ORNL/CP-102910

STAINLESS STEEL FOIL WITH IMPROVED CREEP-RESISTANCE FOR USE IN PRIMARY SURFACE RECUPERATORS FOR GAS TURBINE ENGINES

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ABSTRACT

Primary surface recuperators (PSRs) are compact heat-exchangers made from thin-foil type 347 austenitic stainless steel, which boost the efficiency of land-based gas turbine engines. Solar Turbines uses foil folded into a unique corrugated pattern to maximize the primary surface area for efficient heat transfer between hot exhaust gas on one side, and the compressor discharge air on the other side of the foil. Allegheny-Ludlum produces 0.003 - 0.0035 in. thick foil for a range of current turbine engines using PSRs that operate at up to 660°C. Laboratory-scale processing modification experiments recently have demonstrated that dramatic improvements can be achieved in the creep resistance of such typical 347 stainless steel foils. The modified processing enables fine NbC carbide precipitates to develop during creep at 650-700°C, which provides strength even with a fine grain size. Such improved creep-resistance is necessary for advanced turbine systems that will demand greater materials performance and reliability at higher operating conditions. The next challenges are to better understand the nature of the improved creep resistance in these 347 stainless steel foil, and to achieve similar improvements with scale-up to commercial foil production.

Introduction

The Primary Surface Recuperator (PSR) was originally devised by engineers at Caterpillar in the 1970's, and is utilized extensively today on land-based gas turbines produced by Solar Turbines, and by others[1]. The PSR is a compact heat-exchanger that recovers exhaust heat from the gas-turbine, and transfers it to the compressor discharge air, so that combustion takes place with preheated air (Fig. 1). This requires less fuel to produce the turbine's power and substantially improves its net thermal efficiency. The PSR is made of thin foils from type 347 austenitic stainless steel (Table 1), folded into a uniquely designed pattern to maximize the primary surface area in contact with the exhaust gas and compressor air for efficient heat

transfer. Such folded sheets are welded together in pairs to form "air cells", which then are assembled together to make up the core of the recuperator. A smaller air-cell unit tested in a Capstone microturbine engine is shown in Figure 2a, and a cross-section cut from a new, larger air-cell is shown in Figure 2b. This unique PSR design enables each air cells to flex freely to avoid stress build-up, and improves their resistance to cyclic thermal fatigue. The PSR design is 30% smaller than other kinds of recuperator technology[1], including plate-fin and tube-shell designs. It also removes the restraints on start-up times, which can be about the same with the PSR as for simple gas-turbines without recuperators.

The PSR uses fine-grained type 347 austenitic stainless steel, much finer than the 50-100 μm grain sizes typical of such stainless steels used in boiler tubing or other larger component technology. If stresses or temperatures go beyond the design limits, creep can occur which then deforms the material (Fig. 3). It is, therefore, desirable to improve the creep-resistance of such type 347 stainless steel foil through processing modification and/or in-grade minor compositional modifications. New Advanced Turbine System (ATS) engines will demand greater performance of the materials used in high-temperature, compact heat-exchangers. Understanding how to consistently achieve improved creep-resistance in 347 stainless steel or other stainless alloy foils is an important technology goal of this work.

Background on Alloy Development in Austenitic Stainless Steels for Improved Creep-Resistance

The initial ideas for this alloy development work came from over 15 years of alloy development work directed toward radiation-resistant steels[2-5]. These ideas then led directly to the discovery that unique, ultrafine MC carbide dispersions could be produced and stabilized, to significantly improve the creep-rupture resistance of austenitic stainless steels and alloys at 700-800°C. The driver for this prior work was developing austenitic stainless steels (type 316 and other closely related alloy

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compositions) which could resist radiation-induced void-swelling and grain-boundary helium-bubble embrittlement during long-term exposure in either a fast-breeder or magnetic fusion reactor component environment. Briefly, void swelling resistance, particularly in simulated fusion reactor environments, was directly related to the formation and stability of very fine MC carbide particles within the grains. Grain boundary helium embrittlement resistance was directly related to the formation and stability of similar MC carbide particles at the grain boundaries. In both of these cases, the beneficial effect of such finely dispersed MC carbide precipitates was directly related to the trapping of an even finer dispersion of very tiny helium bubbles at their interfaces. Such MC carbides were most effective when they formed during irradiation from an initially uniform solid solution matrix with heavy concentrations of dislocation networks from prior cold-work (20-25%). The critical, life-limiting phenomena was then the resistance of such fine MC carbides to dissolution and coarsening. When such MC carbide structures became unstable during reactor irradiation, their beneficial protection was lost, and both void swelling increased and grain-boundary helium embrittlement became worse. In summary, this scientific, microscopic analysis established a clear connection between the control of microstructural mechanisms and the control of critical properties behavior. This method of designing and controlling the in-service microstructure is also useful as an alloy development tool for other applications.

The initial work required the development of finer and more stable MC carbide dispersions in a 14Cr-16NiMoMn austenitic stainless steel matrix (Table 1). It was found by using sophisticated microcompositional analysis techniques that very fine (2-5 nm) Ti-rich MC particles contained very high levels of Mo and/or Cr, and that these two elements diminished as the MC particles grew and then became mainly Ti-rich[6-8]. Similar studies of Nb-rich MC carbides showed them to contain primarily Nb whether large or small. The search for the effects of combinations of minor alloying additions showed that V additions had very strong synergistic effects when added with Ti to reduce the amounts of Cr and Mo contained in fine MC carbide particles. Furthermore, the triple combination of Ti+V+Nb additions was found to be even more effective in reducing the Cr and Mo contents of tiny MC carbide particles. In turn, those fine MC distributions became much more stable than steels with only single or double alloying additions[7].

Another important component of the alloy development work for reactor applications was an emphasis on tailoring the complex precipitate microstucture at the grain boundaries. This comprehensive study of alloying effects on the precipitate phases that developed during reactor irradiation or during long-term thermal aging produced a set of "rules" for solute additions to control and stabilize the formation of fine MC carbides, as well as to prevent the formation of other undesirable intermetallic phases in the austenite grain boundaries or matrix. These "rules" for solute effect include: a) *reactant effects* - Ti, V, Nb and C are added to directly form the fine stable MC carbides with minimum amounts of undesirable Cr or Mo; b) *catalytic effects* - positive and negative controls, with added solutes like B and P which enhance carbide formation (especially MC carbides) being positive, and solutes such as Si and Nb, or Ti which enhancing the formation of Laves and σ phases, respectively, being negative; c) *inhibitor effects* - these are subtle effects in which certain elements block or retard the formation of particular phases, particularly if those elements are rejected by the phase as it forms. An extremely powerful effect for combinations of solutes to minimize or eliminate intermetallic phases. Ni retards σ and Laves phase formation, and the minor additions of B and C together have very strong retarding effects on those phases; d) *interference effects* - controlling or minimizing the competition of various phases for a common element (ie.,Ti in TiN and TiC) is important for decoupling complex phase behavior, so that a single phase (like MC carbides) can be isolated, and then fine-tuned for optimum effects in the alloy.

The modified 14Cr-16NiMoMn steels, optimized for reactor applications, were also found to have outstanding creep-strength and rupture-resistance at 700°C when tested for potential boiler tubing applications for coal-fired steam power plants[6,9,10]. These new steels developed extremely fine, stable MC carbide structures during creep-testing, which made them very strong (Fig. 4). Thus, they were called high-temperature, ultrafine precipitate-strengthed (HT-UPS) steels. The HT-UPS steels were also sensitive to changes in processing conditions. Optimum creep-resistance was only found when higher solution-annealing temperatures (1150-1200°C) and small (2-5%) amounts of prior cold-strain were used[11,12]. The best steels showed less than 1% creep at 700°C/100-140 MPa for times of 30,000 to 50,000 h, without rupture (Fig. 5)[9,10]. These HT-UPS steels were always stronger with small amounts of cold- or hot-work relative to the solution-annealed (dead-soft) condition, and actual tube-component tests were as good as or better than smaller specimen tests. These HT-UPS stainless steels were generally stronger than the best comparable austenitic stainless steels and alloys[13] (including 17-14CuMo, Esshette 1250, and even NF709, Table 1 and Fig. 6), and were comparable to many Ni-based superalloys. Their creep-strength was directly related to the robust, ultrafine MC carbide structures that developed rapidly and then resisted coarsening or dissolution during long-term creep. Their extremely long secondary creep regime was directly related to their resistance to the microstructural damage mechanisms that usually trigger the onset of teriary creep or rupture, including resistance to creep-void formation, resistance to the formation of embrittling intermetallic phases (σ, Laves), and resistance to localized recrystallization and softening[10]. Despite their strength, they also had a ductile failure mode, which also gave them excellent resistance to creep-crack growth. Their primary drawback for boiler tube applications was that with only 14wt.% Cr, their oxidation resistance was relatively poor, and they needed to be clad with more corrosion-resistant alloys for protection, which is more difficult and expensive. The alloy development principles and concepts, however, were general, and were also successfully applied to produce other HT-UPS austenitic materials, including a modified 800H stainless alloy, and a Fe-Cr-Mn stainless steels[14,15].

Laboratory-Scale Foil Processing For Improved Creep-Resistance

All of the above results were generally obtained for nderstabilized stainless steels and alloys, processed into tubing r plate with grain sizes typically 100 μm or more. In the fnited States today, most coal-fired boilers use type 304H instabilized) or 347H (fully-stabilized) for superheater pplications[9]. Sumitomo has developed a special kind of rocessing to produce fine-grained (about 25 μm grain size) 47H superheater tubing, which exhibits both improved orrosion resistance (steam- and fire-side) and improved creep-ipture strength relative to typical products of that grade of teel[16]. But even fine-grained 347H still has much less creep-trength than the advanced austenitic stainless steels and alloys eveloped specifically for creep-resistance (Fig. 6). Moreover. tainless steels foils that are 0.003 to 0.004 in. (0.076 to 0.102 im) thick typically have grain sizes of 10 μm or less (to rovide at least 10 grains across the foil thickness), and finer rain sizes tend to reduce rather than enhance creep resistance. umitomo processing to produce fine-grained 347H superheater ibing involves a solution annealing step at 1300°C or above, rior to the last two cold-deformation and annealing steps, and enerally such high-temperature processing is not feasable for roducing thin foil products[16]. Therefore, the first challenge this ndustry/national laboratory collaborative project addressed was - *evise a modified foil processing method to improved the creep esistance of fine-grained 347 stainless steel foil*. The typical reep strain behavior of standard commercially-produced foil of i47 stainless steel at 732°C and 48.3 MPa is shown in Figure '. The desired target goal for improved creep-resistance is also ndicated.

Several different modified processing methods were levised which varied short-time annealing at higher temperatures o partially dissolve NbC particles, present from prior hot-band >rocessing, before the final recrystallization anneal, which is equired to establish the final grain-size. Small pieces of foil vere cold-rolled and then annealed in a special radiant-heating urnace (high-intensity tungsten-halogen lamps in an Ar-4%H$_2$ itmosphere) facility at ORNL, to more effectively simulate the apid heating and cooling, and the non-oxidizing (or reducing) itmosphere found in typical commercial-scale, continuous-innealing-lines (CALs). Intermediate CALs have an oxidizing itmosphere, with subsequent descaling and acid pickling 'estoring the bright surface. Final CALs are bright annealing ines with reducing hydrogen atmospheres.

Creep specimens were cut from the 0.004 - 0.0045 in. hick foils and tested in air at 732°C and 48.3 MPa, and the first est results obtained indicated that dramatic improvements in :reep-resistance are possible using several different modified >rocessing conditions. These intitial creep results far exceeded he initial target goals set for this project (Fig. 7), but must be :onfirmed by follow-on experiments, and more thoroughly :haracterized by expanding the testing to other temperatures and tresses. These initial creep-tests are still in progress, together

with other creep tests at different stresses at 650-730°C. It is. however, noteworthy that the 347 steel foil with modified processing only shows about 1% strain at 732°C after about 5000 h.

Scale-Up Issues For Commercial Foil Processing

One of the most profound changes in materials processing over the last 25 years has been the change from batch annealing to continuous annealing processes for many different product forms. Modern state-of-the-art sheet and foil production is sophisticated, high-speed processing technology that produces a much more uniform product, with controlled and consistent microstructure (mainly grain size) and properties (mainly tensile properties). A typical commerical-scale intermediate CAL at an Allegheny-Ludlum rolling-mill facility is shown in Fig. 8. The length from front-to-rear is almost a city block. Coils (typically 7-11 tons) from previous cold-rolling (50-75%) are unrolled and passed through an annealing furnace for a flash anneal (less than 15 seconds in the hot-zone and only several seconds at the peak temperature) to produce a fully-recrystallized, fine-grained structure suitable for further cold-rolling to reduce the thickness, and then are recoiled at the end of the line. The challenge facing this project now is to develop a modified processing method for standard grade 347 austenitic stainless steel that can be applied to modern CAL equipment, given the real equipment constaints for adjusting the annealing times and temperatures. Scale-up production trials for some of the 0.004 in. thick foil needed for the manufacture of new PSR air-cells for the Mercury 50 ATS are planned. The next steps will be critical tests to determine if the boost in creep resistance observed for laboratory-scale simulated CAL processing can also be achieved in production-scale foil or folded PSR air-cell components. Finally, it is also necessary to balance the costs of processing changes with the improvements in component performance achieved, to obtain the most cost-effective improvements.

Summary

In summary, recuperation is an important part of acheiving maximum performance from ATS engines. A modified processing method that produces 347 stainless steel foils that are more creep-resistant will increase designer's capability to maximize the cost-performance relationship of the PSR. Initial laboratory-scale experiments clearly demonstrate that dramatic improvements in creep-resistance can be achieved using processing parameters relevant to commercial CAL processing. Putting sufficient NbC precipitates into solution during processing should enable finer NbC to precipitate during creep, but further characterization analysis of the specimens currently in-test now is needed to demonstrate that. Processing to improve the creep-resistance of fine-grained foils will also have wider benefits to other engine technology applications, including recuperators for micro-turbines, and possibly other

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applications (ie. automotive heat-shields and flexible couplings) for austenitic stainless steel foils and sheets.

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Table 1 - Compositions of Various Austenitic Stainless Steels and Alloys (wt.%)

| Alloy	Cr	Ni	Mn	Mo	Si	C	N	Nb	P	Others
typical wrought thicker-walled boiler tubing steels and alloys										
type 316 SS	16-18	10-14	<2	2-3	<1.0	<0.08	<0.1	<0.05	<0.045	
17-14 CuMo SS	16.3	14	0.8	2.0	1.0	0.1	-	0.45	-	3 Cu, 0.2 Ti, 0.07 V
TP347H SS	17-20	9-13	<2	-	<0.75	<0.1	-	<1.0	<0.4	
HT-UPS mod.316	14-16	16	2	2.5	<0.4	<0.1	<0.02	0.1	<0.07	0-2 Cu, 0.3 Ti, 0.1-0.5 V, <0.007 B
310HCbN	24.8	20.3	1.2	0.01	0.41	0.06	0.23	0.54	0.03	
NF709	20.0	25.6	1.0	1.55	0.44	0.1	0.14	0.3	.0.03	0.03Ti, 0.003B
alloy 800H	20	30	0.9	-	0.24	0.08	-	-	-	0.4 Ti, 0.4 Al
HT-UPS mod.800H	20.5	30.5	2.0	2.0	0.22	0.09	0.01	0.24	0.03	0.36 Ti, 0.52 V, 0.01 B
typical recuperator foil steels										
type 347 SS (heat cert. 41271)	17.8	10.2	1.7	0.2	0.6	0.04	-	0.68	0.025	0.24Cu
type 347 SS (heat AL 848691)	17.6	9.7	1.5	0.34	0.5	0.03	-	0.62	0.034	0.28 Cu, 0.003 Ti, 0.071 V

347 Stainless Steel
Recuperator
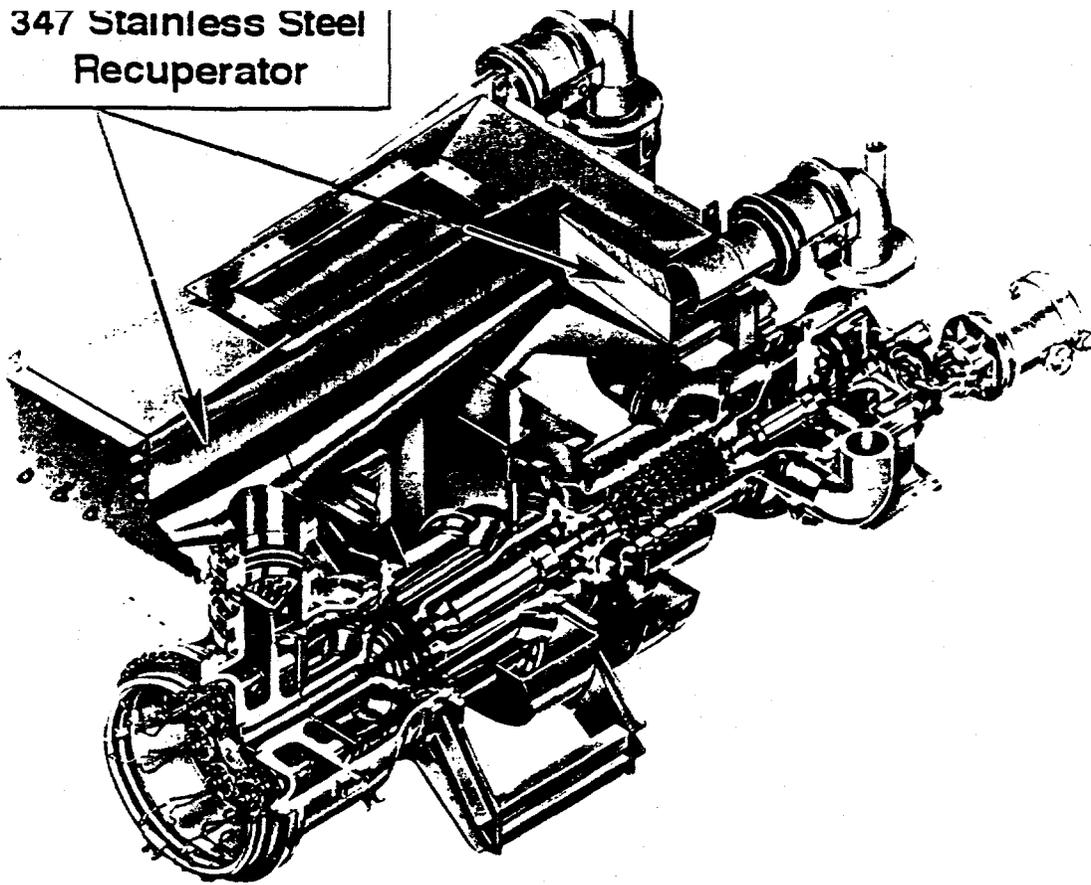
Figure 1 - Cutaway of the design of the Solar Turbines Mercury 50 ATS engine, showing the primary surface recuperator (PSR) above the gas-turbine engine. This is a unique design, with the flowpath for turbine inlet and exhaust matched to the PSR.
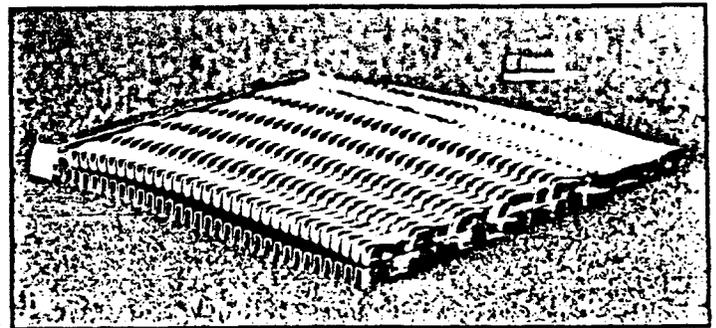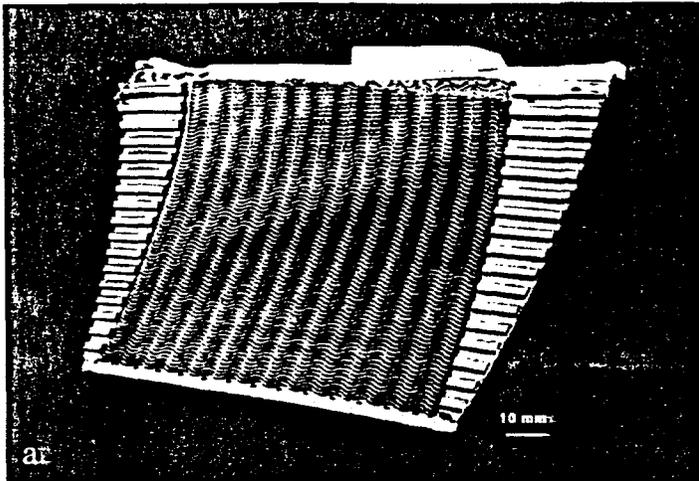

Figure 2 - a) A smaller manufactured 347 stainless steel foil air-cell, the basic repeat unit of the PSR, removed after short-term microturbine engine-testing, and b) a cut-away cross-section of as-manufactured air-cell showing the two folded foils sealed at the end.
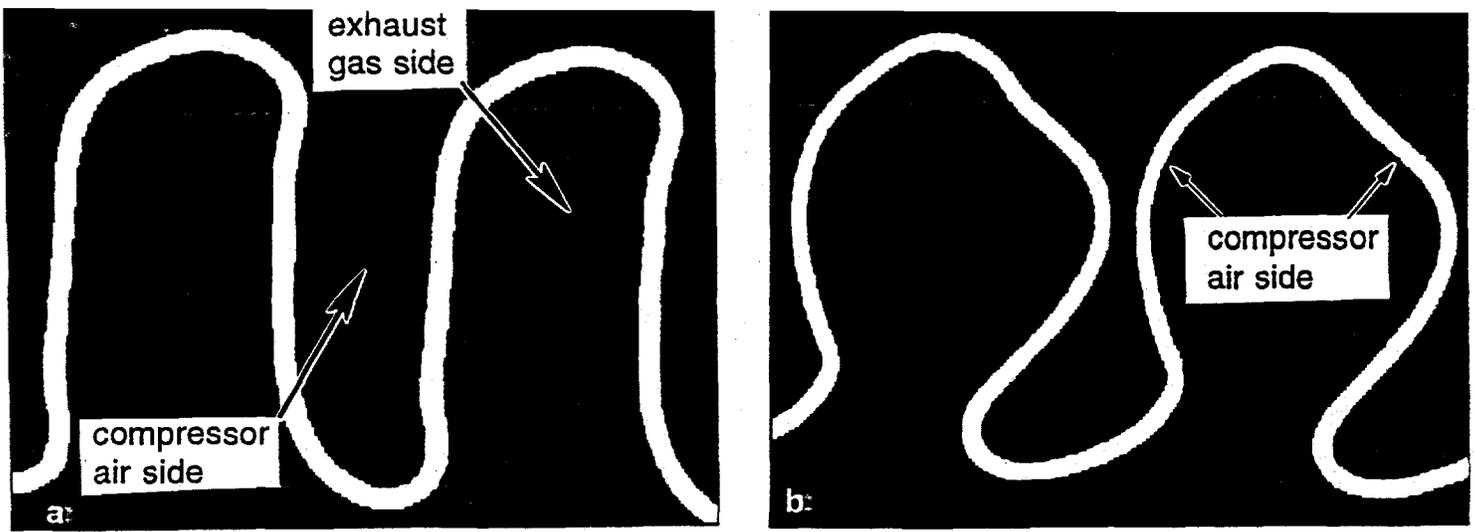
Figure 3 - a) Cross-section of a typical fresh folded 347 stainless steel foil prior to service, b) after creep deformation due to increased stresses that can restrict the airflow paths to limit the component lifetime.
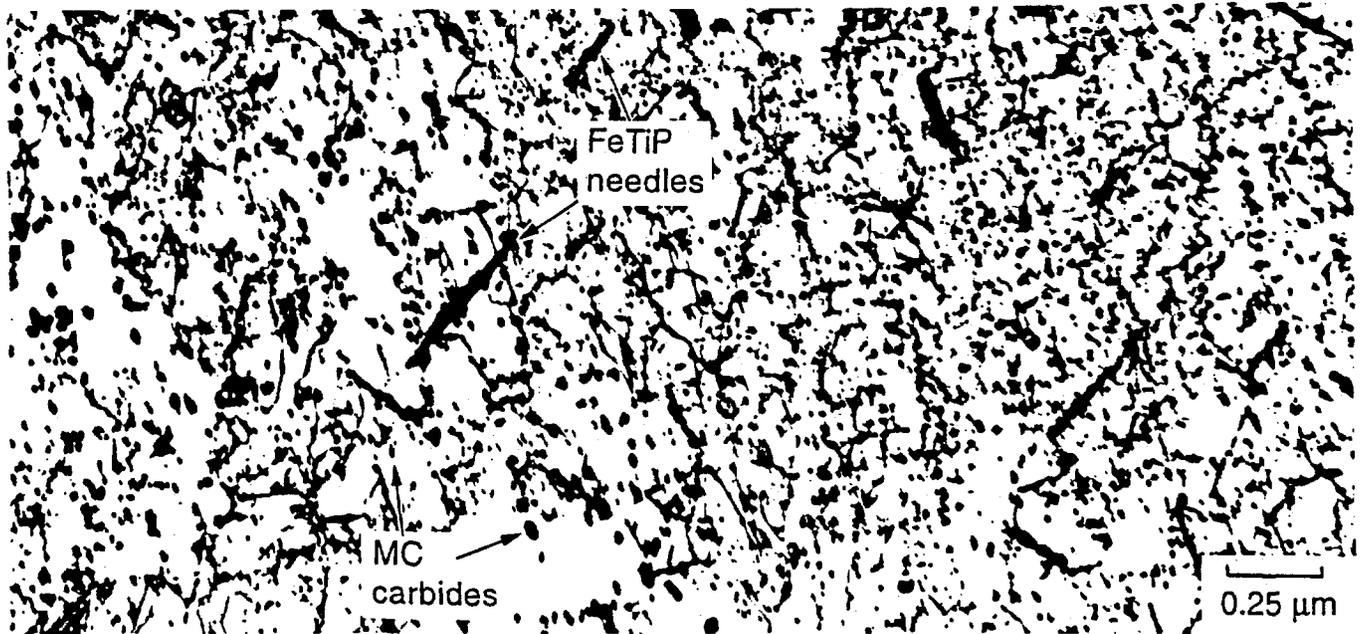

Figure 4 - Transmission electron photomicrograph of ultrafine (Ti,V,Nb)C carbide and FeTiP phosphide precipiates that develop during creep of HT-UPS modified 316 stainless steel at 700°C and 170 MPa (rupture after 18,000 h), which are the basis for its outstanding creep-resistance.
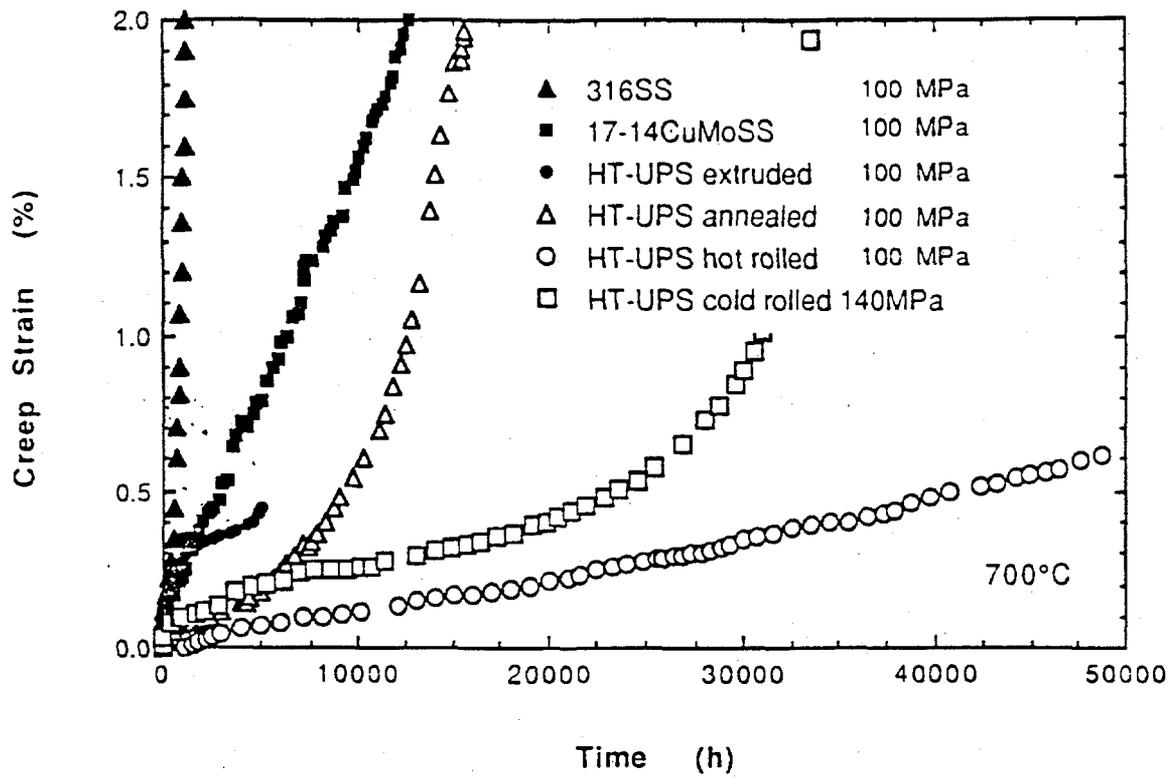
Figure 5 - Creep strain versus time curves plotted for various wrought austenitic stainless steels, including type 316, 17-14 CuMo, and the HT-UPS modified 316 steels (see Table 1), creep tested at 100-140 MPa at 700°C.
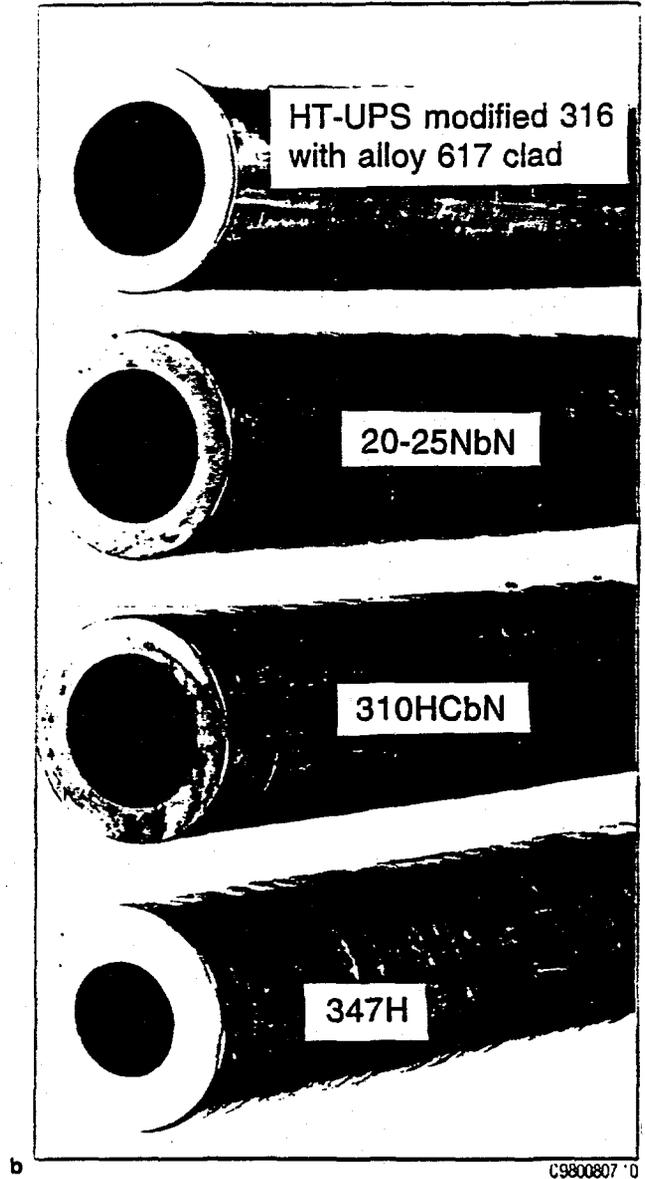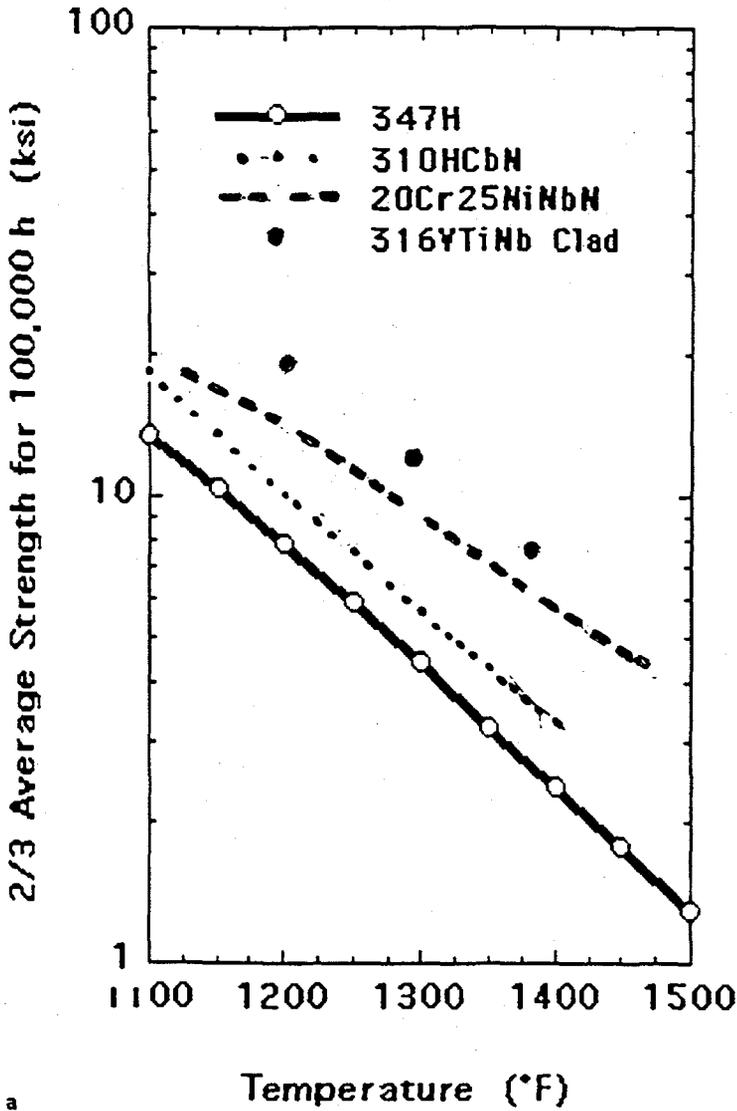
Figure 6 - a) Design stress for superheater tubing (2/3 of the average 100.000 h creep-rupture strength) plotted versus metal temperature for several different austenitic stainless steels and alloys. b) shows the various tubes, with the triply-stabilized HT-UPS modified 316 steel having a thin co-extruded cladding of alloy 617 for fireside corrosion protection, and the others being monolithic alloy tubes. The tubes are ranked in order of strength from bottom (weakest) to top (strongest). The penalty for lack of creep-strength is seen in the thicker tube wall, and hence reduced inner diameter for steam flow.
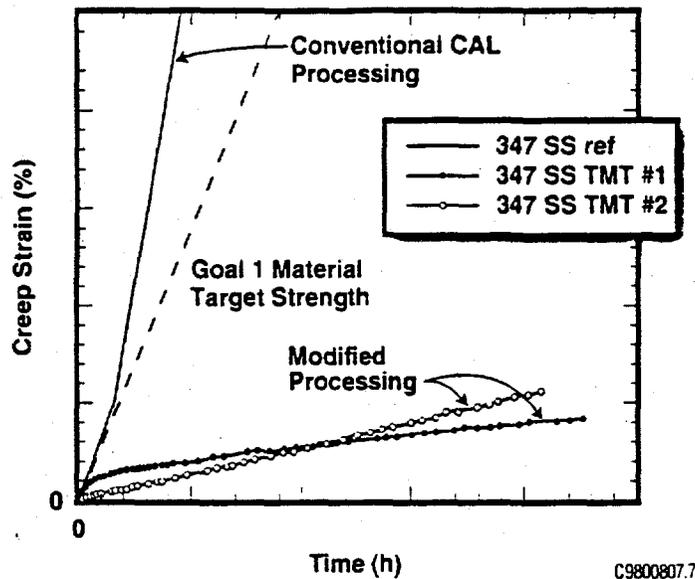
Figure 7 - Creep strain versus time curves for typical 0.0035 in. thick foil of type 347 stainless steel produce by commercial CAL processing. Also included are the target improvement in creep strength for this project. and creep curves obtained from two different modified processing schedules used to produce 0.0042-0.0045 in. thick foil of 347 stainless steel (AL heat 848691, Table 1) in the initial experiment done at ORNL. Creep-testing is done at 732°C and 48.3 Mpa, and this plot has maximum strain values of about 5% and maximum time values of about 5000 h. Clearly, both of the initial modified processing trials show excellent creep-resistance.
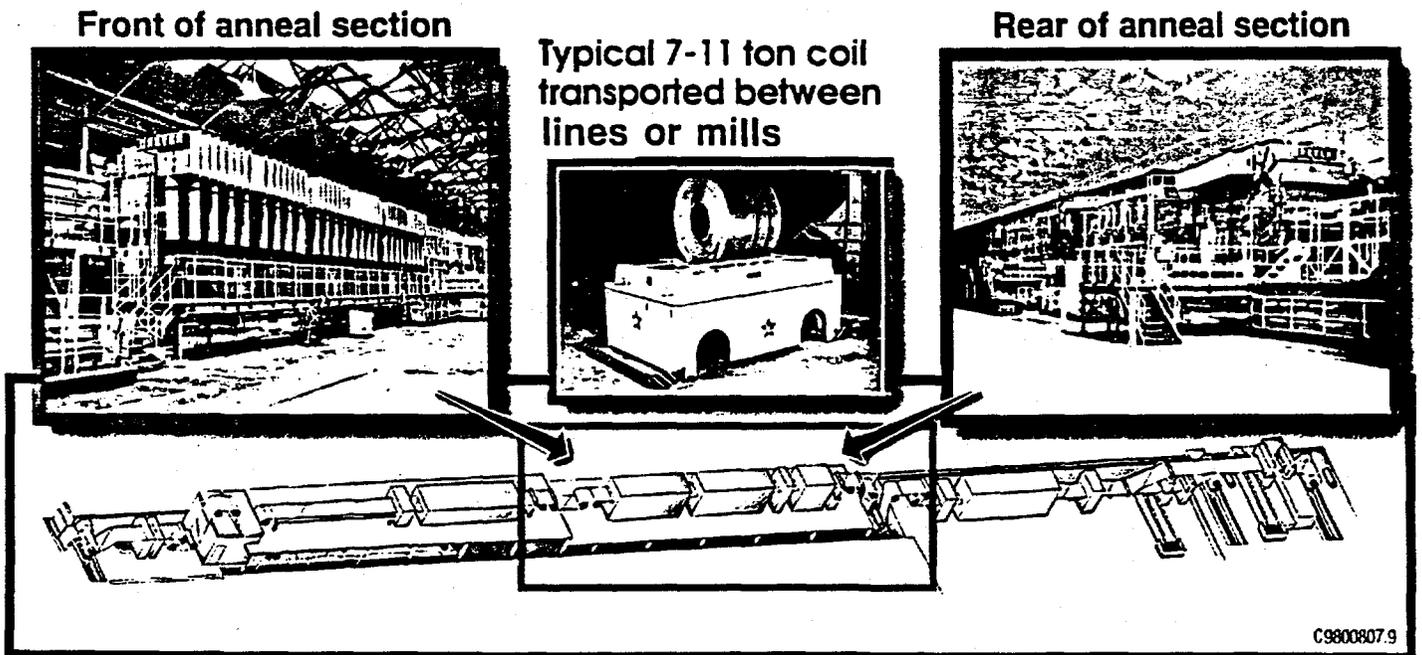

Figure 8 - A typical modern, state-of-the-art intermediate continuous annealing line (CAL) used for commercial stainless steel foil production. The actual CAL line is nearly a city block long, and a typical coil of steel processed at one time will be about 7-11 tons. Four such CAL lines would be involved in reducing a typical stainless steel hotband down to final gage foil. The particular CAL shown is from line #91 at the Vandergrift, PA Mill of Allegheny-Ludlum, an Allegheny-Teledyne Co. The enlarged pictures are the front and rear sections of the annealing furnaces outlined near the center of the lower picture.