Metals and Ceramics Division

CRADA FINAL REPORT
FOR
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EVALUATION OF STAINLESS STEELS FOR PRIMARY SURFACE RECUPERATOR APPLICATIONS

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Abstract

In 1996, a Cooperative Research and Development Agreement (CRADA) was undertaken between the Oak Ridge National Laboratory (ORNL) and Solar Turbines Incorporated to develop improved stainless steels for gas turbine recuperator applications. A team was assembled that consisted of materials and fabrication specialists from ORNL, Solar Turbines, Allegheny Ludlum Research Laboratory, and the University of California-San Diego. The development strategy was to (1) identify the materials performance requirements needed for long-time operation of a recuperator with inlet gas temperatures higher than current practice, (2) select candidate commercial and near-commercial alloys with potential for meeting the performance requirements, and (3) optimize thermal-mechanical processing to meet commercial production capabilities. The performance requirements were incorporated into three categories (fabricability, corrosion resistance, and mechanical strength) and teams were assigned to address each of these issues. The composition of the steels under consideration ranged from 18 to 25% chromium and from 8 to 25% nickel. Foils of thicknesses in the range 0.08 to 0.12 mm were produced by laboratory processing and by commercial processing. Thermal-mechanical processing was varied to obtain a range of grain sizes or to vary other physical metallurgical parameters. Oxidation experiments were undertaken in laboratory air and air with controlled water vapor contents at ORNL, Allegheny-Ludlum, and the University of California San Diego. Cyclic oxidation testing was included. Testing conditions were selected to enable models to be developed that included temperature, time, water content, and foil thickness as variables. Creep testing was performed in the temperature range of 677°C to 732°C for times extending beyond 10,000 h at ORNL and Solar Turbines. Optical, scanning, and analytical electron microscopy were used to examine the evolution of microstructure during aging, corrosion, and creep exposures. Based on the experimental work, optimized compositions and thermal-mechanical processing specifications were developed.

Objectives

Two goals were defined for the CRADA. Goal 1 was to modify the chemistry and processing of 347 stainless steel to permit longer-time operation at gas inlet temperatures to as high as 650°C. Specific objectives included a model to predict life a demonstration of tolerance to cyclic operation, an improvement in oxidation resistance, and an improvement in creep strength. Goal 2 was to develop a steel with performance characteristics comparable to 347 stainless steel but for even longer operation at gas inlet temperatures in excess of 650°C. Specific operating times and pressures fall within the category of CRADA Propriety Information (CPI) and will not be identified.

Benefits

The successful completion of this CRADA and the achievement of the CRADA objectives were judged to be beneficial to the original program sponsors and projects. Additional beneficiaries include new DOE-funded programs such as VISION 21 programs supported by Fossil Energy and Distributed Power programs supported through the microturbine research by the Office of Industrial Technologies.

Work Performed

To achieve the CRADA objectives, three research teams were organized. One team concentrated mainly on alloy design, manufacturing, and microstructural evaluation. The second team focused on oxidation and other environmental effects. The third team examined high-temperature mechanical performance. Each team included representatives from the two CRADA partners. Consultants and a material producer (Allegheny Ludlum) provided additional input. The teams interacted and integrated the data to determine the overall project direction.

Alloy design, fabrication, and metallurgical evaluation

More than fifteen commercial and developmental stainless steels were examined. Commercial steels were selected for their known oxidation resistance, strength, or combination of properties. Most often, these commercial steels were available as relatively coarse-grained wrought products. Chromium, needed for oxidation resistance, ranged from 17 to 25 percent, while nickel, needed for strength, ranged from 8 to 25 percent. Within grade restrictions were placed on the commercial steels to optimize performance. Developmental steels had Cr contents greater than 347 stainless steel, and compositions were selected to improve their strengths relative to standard 347 stainless steel. All steels contained strong carbide formers, such as titanium, vanadium, niobium, and tantalum. Reactive element contents ranged from hypo-stochiometric to hyper-stochiometric with respect to carbon content. Some steels contained additions favorable to improve oxidation resistance. These elements included aluminum, silicon, zirconium, yttrium, and cerium. The exact chemistries were considered to be CPI and will not be identified here.

The commercial and developmental steels were procured as a variety of product forms and then rolled to foil using laboratory-scale processing at ORNL. The determination of optimum production schedules was a major undertaking and was guided by the need to meet microstructure, strength, and fabricability goals. The degree of thickness reduction between anneals was examined as well as the annealing temperature and time. The annealing procedure was varied to allow control of the heating rates, hold times, and cooling rates in order to represent various commercial continuous annealing line (CAL) capabilities. Post annealing treatments included "leveling" stretching, and tensile straining. Final thickness for the foils ranged from 0.08 to 0.12 mm. Typical values for the ASTM grain size numbers ranged from 8 to 12. Details of the fabrication studies fell within the category of CPI and will not be identified here. The same is true for the restricted chemistry of commercial 347 stainless steel foil.

Optical microscopy was used to determine grain size and its variation with thermal-mechanical processing. Scanning electron microscopy (SEM) and analytical electron microscopy (AEM) were used to characterize materials at different critical steps in the production schedule as well as in the final condition. The relationships between fabrication schedules and metallurgical phenomena such as recrystallization, carbide solution, and carbide precipitation were examined for several of the more promising steels. It was found that a wide range of metallurgical conditions could be produced in the foils and it was possible to achieve fine grain sizes stabilized by fine grain-boundary precipitates for good long-time stability. Details of the optimized metallurgical microstructures fell within the category of CPI and will not be provided here.

Oxidation studies

The oxidation studies were designed to provide data that would lead to a life prediction model. Environmental considerations included time, temperature, and moisture content. Metallurgical considerations included composition, microstructure, and scale formation characteristics. Mechanical considerations included foil thickness, surface finish, and surface contour.

Oxidation testing was performed at ORNL, Solar Turbines, Allegheny Ludlum Research Laboratories, and the University of California San Diego. Oxidation temperatures ranged from 650 to 900°C and times ranged to beyond 20,000 hours. Moisture contents ranged from laboratory air to 15% water. Both static and cyclic testing was performed with typical cycling rates of once per day and once every four days. Weight changes were monitored. The time to break away corrosion was a critical measurement.

Detailed microstructural investigations were undertaken of the exposed coupons. The influence of composition and exposure conditions on scale formation was examined as well as the changes in the substrate chemistry. For the case of type 347 stainless steel, comparisons were made to scale characteristics of service-exposed components.

A model was developed for life prediction of 347 stainless steel. Life, based on the time to break away oxidation, was predicted as a function of service temperature and water vapor content. Parametric values developed for the model fall within the CPI category. Work was begun to extend the model to steels with higher chromium contents than 347 stainless steel.

Mechanical behavior

An extensive high-temperature mechanical testing program was undertaken at ORNL and Solar Turbines. The purpose was to assess the effectiveness of various compositions and thermal-mechanical processing schemes in producing a foil that would meet the mechanical performance goals established by the CRADA for service at 650 and 704°C. Performance was based on creep resistance rather than stress rupture to insure best relevance of test data to in-service component behavior, hence minimum creep rate and the times to specific creep strains were the data of most interest.

Specimens from more than fifteen different heats of steel were tested. In addition, up to six different thermal-mechanical conditions were examined for some compositions. Most of the creep testing was in the temperature range of 650 to 732°C (1200 to 1350°F). Testing time ranged from a few hours to more than 30,000 hours. About 25 creep machines were used and more than 500,000 machine-hours of creep testing were completed.

Significant differences in strength of the foils were observed. First, judicious thermal-mechanical processing was found to be highly significant in promoting good performance. Creep strength increased with increasing grain size, as expected, but processing to stabilize grain boundaries and dislocation networks by fine precipitates was also important to creep strength. When combined with restricted chemistry versions for the steel, the thermal-mechanical processing was especially effective. For example, the optimized thermal-mechanical processing condition for type 347 stainless steel produced a foil with nearly twice the strength of the "standard" foil. Second, alternate compositions could be processed to produce strengths that exceeded that for the optimized 347 stainless steels. This produced a combination of strength and oxidation resistance with the potential of meeting the CRADA goal.

Inventions

The CRADA partners identified several possible inventions related to either alloy composition or processing. A decision was made not to proceed with patent applications. This decision was partially based on the concern of the Allegheny Ludlum participants that their proprietary fabrication procedures would be disclosed in the patent information.

Commercialization Possibilities

A commercial heat of restricted chemistry 347 stainless steel foil was ordered by Solar Turbines. This material is intended for a test recuperator. Included in the order is a request for special processing that should improve mechanical performance.

A small heat of a stainless steel with enhanced properties relative to 347 stainless steel was ordered for commercial processing to foil following an optimized fabrication procedure.

Plans for Future Collaboration

Based on this CRADA Solar Turbines, ORNL, and Allegheny Ludlum have entered into a new agreement to further develop primary surface recuperators for advanced microturbine applications. In the program, supported by the DOE Office of Industrial Technologies, the use of the enhanced strength stainless steels will be extended to service temperatures of 670°C.

Two additional research efforts have been undertaken under support of the DOE Office of Industrial Technologies. Both research efforts are aimed at extending the operational limits from metallic recuperators to higher temperatures. Both stainless steels and nickel-based alloys are included. Technology developed in the CRADA concluded here will be used extensively.

Conclusions

Restriction of alloy chemistry and the specification of optimum thermal-mechanical processing schedules produced an enhanced creep strength type 347 stainless steel foil. When produced on a commercial scale the material could extend the operating time or temperature of primary surface recuperators. Sufficient data exist for this material to develop a lifetime predictive model for setting the oxidation-limited service conditions.

Alternative stainless steels can be produced that have better oxidation resistance than type 347 stainless steel. Mechanical properties data for foils with optimized chemistry and thermal-mechanical processing indicate that these steels may further extend the operating temperatures and times for primary surface recuperators.

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