C/ORNL 00-0570

CRADA Final Report
for
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Evaluation of Durable Metallic Supports for Catalytic Combustors

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Catalytica Energy Systems, Inc.

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Prepared for
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Gilbert, Arizona

Prepared by
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TECHNICAL DISCUSSION

Abstract

In 2000, a Cooperative Research and Development Agreement (CRADA) was undertaken between the Oak Ridge National Laboratory (ORNL) and Catalytica Energy Systems Incorporated (CESI) to determine the properties of current metallic catalyst supports and examine new candidate alloys for this application. A team was established at ORNL to examine oxidation-limited lifetime of these thin-walled metallic components using standard lifetime models and to measure the mechanical properties of the foils (40-200μm in thickness) which can differ substantially from bulk properties. Oxidation experiments were conducted on foil specimens at 700˚-1100˚C in laboratory air and in air with 10 vol.% water vapor to better simulate the combustor environment. At the higher test temperatures, time to oxidation-induced (i.e. breakaway oxidation) failure was determined in 1h cycles in order to verify predictions from a standard reservoir-type oxidation lifetime model. Selected specimens were run for >10,000h in 100 or 500h cycles at lower test temperatures in order to determine the oxidation kinetics for the model. The creep properties of selected foils were measured for 4,000-8,000h at operation-relevant stresses and temperatures. None of the new candidate alloys significantly out-performed currently used alloys in laboratory testing, particularly in oxidation lifetime testing. Therefore, engine testing was not performed on any of the new candidate alloys. Both the oxidation- and creep-resistance of FeCrAl alloys was greater than expected and the results of the CRADA allowed CESI to extend life or increase operating temperatures for these lower cost substrate alloys in the next generation of catalyst modules.

Objectives

Three work areas were defined for the CRADA. The first area was investigating the oxidation behavior of current and candidate alloy foils. The goal was to obtain data such as the oxidation rate as a function of temperature and environment, the time to breakaway oxidation at high test temperatures and the residual Al alloy content at breakaway oxidation. These inputs are needed for a standard reservoir-type oxidation model. The second work area was to use the experimental data to model the oxidation-limited lifetime of foil materials as a function of temperature, foil thickness and composition. The third task was to measure mechanical properties, in particular creep rates and creep to failure life, of similar foils at application relevant temperatures and stress levels.

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. The range and accuracy of relevant long-term data for FeCrAl and NiCrAl alloys provided by the CRADA results is of great value for assessing the useful life of current and future catalyst modules. New alternative substrate foil alloys (e.g., ODS alloys) were shown not to offer significant benefits to offset increased materials and fabrication costs. However, the oxidation- and creep-resistance of FeCrAl alloys was greater than expected allowing either life extention with current conditions or an increase in operating temperatures for these lower cost substrate alloys in the next generation of catalyst modules. Additional beneficiaries include DOE-funded programs such as VISION 21 programs supported by Fossil Energy.

Work Performed

To achieve the CRADA objectives, an ORNL team was formed which had expertise in each of the three work areas.

Oxidation Testing

Seven alumina-forming alloys were examined during the course of this testing. Currently used alloys, several commercial alloys and two experimental alloys were tested in foil form (40-250μm) to determine their oxidation kinetics and oxidation-limited lifetime at 700˚-1100˚C in laboratory air and air with 10 vol.% water vapor to simulate the combustion environment. Testing to failure occurred at 1050˚ and 1100˚C in 1h cycles. After testing, the residual Al content was measured in foils which had reached breakaway oxidation using electron microprobe analysis (EPMA) to determine the critical Al content at breakaway. Breakaway oxidation is defined as the time at which a protective alumina scale can no longer be formed on the alloy and accelerated oxidation kinetics are observed.

Oxidation Lifetime Modeling

The experimental data was used to predict long-term performance at lower application temperatures using a standard reservoir-type lifetime model. This model is based on consumption of the available Al reservoir in the alloy and therefore needs the foil thickness and starting and final Al content in the alloy to determine the available Al reservoir. The rate of Al consumption is based on experimentally-determined reaction kinetics. The model lifetime predictions were compared to experimentally determined lifetimes in order to gauge the effectiveness of the predictions. Lifetime predictions were made across a range of application relevant temperatures for each of the alloys tested.

Mechanical Properties Testing

Creep testing of selected foil materials was conducted at several test temperatures and stress loads as specified by CESI. Dead load tests were conducted for 4,000-8,000h in order to obtain application relevant design data. These data were incorporated into semi-empirical models of creep rate for interpolation and modest extrapolation from the test conditions for design purposes.

Testing at CESI

CESI conducted three tasks that supported the CRADA project: (1) A full-pressure (10-bar) cyclic furnace rig was used to expose catalyst foil coupons (NiCrAl) under simulated combustion conditions for 4,000h with 12h short-term excursions to below 400˚C; (2) Two in-engine (KHI-M1A-13X at ~1.5-MW) long-term(4000h and 8000h) full-scale tests of catalyst foils; and (3) Finite-element strain models were developed to assess the stress levels and strain limits of catalyst foils under in-engine flow conditions. CESI also incorporated the ORNL creep rate data into fitted analytical expressions for use in future design work.

Inventions and Commercialization

None of the experimental alloys showed better performance compared to the current candidates. Therefore, no patentable claims were discovered and none of the experimental compositions are expected to be commercialized.

Plans for Future Collaborations

Based on the excellent working relationship developed during the CRADA, ORNL is continuing to work with CESI and other interested parties to determine other mechanical properties of foils and to characterize engine exposed foils to confirm the lifetime models.

Conclusions

The physical properties of current and candidate alloys for catalyst supports were examined. Using a standard oxidation life model, lifetime as a function of foil thickness, starting Al content and oxidation temperature were modeled for candidate alloys using experimentally determined data. Model predictions were tested using experimental data obtained at 1050° and 1100°C. The experimental and model results indicated that none of the experimental compositions were clearly superior to currently used commercial alloys. The results found that current alloys were more oxidation- and creep-resistant than previously assumed. Therefore, none of the new materials were exposed to engine testing. Creep testing of foils was conducted for 4,000-8,000h on selected foils at application relevant temperatures. This data will be used in design-relevant models to assist in the design of new catalyst supports with improved durability.

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