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CRADA Final Report
for
CRADA Number ORNL94-0325

IMPROVING THE OXIDATION RESISTANCE IN ADVANCED SINGLE CRYSTAL NICKEL-BASED SUPERALLOYS FOR TURBINE APPLICATIONS

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Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
Lockheed Martin Energy Research
Corporation
for the
U.S. Department of Energy
under contract DE-AC05-96OR22464

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Improving the Oxidation Resistance in Advanced Single Crystal
Nickel-based Superalloys for Turbine Applications

CRADA No. ORNL94-0325
between
Pratt and Whitney Division
and
Oak Ridge National Laboratory

Abstract

The focus of this project was the examination of the role of yttrium and other alloying elements on the microstructure and oxidation performance of improved single crystal nickel-based superalloys for advanced turbine applications. The microstructure and microchemistry of both base and modified alloys and their surface oxides have been measured with state-of-the-art microanalytical techniques (atom probe field ion microscopy and electron microscopy) and then correlated with burner rig and engine-test oxidation performance. The overall technical goals included; (1) identifying the partitioning behavior of the elemental additions in these superalloys before and after burner rig and engine tests and the effect on the misfit energy between the phases in the alloys; (2) examining the oxidation performance of these newly-developed alloys; (3) identifying the influence of pre-oxidation processing on the subsequent oxidation performance; and (4) relating the microstructural and microchemical observations to the observed performance of these superalloys. The comparison of the base and modified alloys will produce a better understanding of the interaction between chemistry, structure, and performance in superalloys. In addition, it will lead to optimized alloys with improved performance including enhanced durability in the operating environments at the elevated temperature required to improve energy efficiency. The availability of alloys capable of higher temperature operation will minimize the need for expensive coatings in extreme temperature applications.

Through funding of this CRADA by ER-LTR Program, DOE has realized several benefits from this project; a number of which arise from strengthening the knowledge base at both ORNL and Pratt & Whitney on high temperature oxidation and creep of superalloys. There are several other programs active at ORNL that will directly or indirectly benefit from the knowledge and experience gained under this CRADA, including the Mechanically Reliable Surface Oxide (MRSOX) Project under the DOE Basic Energy Sciences (BES) Synthesis and Processing Center, the DOE Energy Efficiency Advanced Turbine Program, the Corrosion Science base program, and the BES Microscopy and Microanalytical Sciences task. In addition, DOE has provided access to the outstanding and often unique characterization facilities and associated technical expertise at ORNL to Pratt and Whitney, a major American manufacturer, which will benefit their economic competitiveness.

This work was supported through a CRADA with Pratt & Whitney, East Hartford, Connecticut, sponsored by the Laboratory Technology Research Program, Office of Science, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation.

Technical Discussion of CRADA

As their portion of this CRADA (No. ORNL94-0325), Pratt and Whitney (P&W) provided a number of modified versions of their advanced superalloy in both before and after oxidation conditions. Both rare earth additions and trace element additions were included in the alloys provided, as well as the base alloy. A desulfurized alloy was also supplied by P&W. The oxidized specimens included either furnace or burner rig exposures of test samples or actual turbine blades. Both isothermal and cyclically oxidized specimens were provided. In addition, P&W provided the results of the oxidation tests including gravimetric and scale adherence measurements, as well as performance results from engine testing. ORNL provided high spatial resolution microstructural and microchemical characterization of both the as-processed alloys and the oxidized specimens. This characterization included scanning and transmission analytical electron microscopy (AEM), atom probe field ion microscopy (APFIM), and atom probe tomography (APT) of these specimens. Scanning electron microscopy (SEM) of both the as-processed and oxidized materials provided both microstructural and microchemical characterization of these complex alloy and oxide scale structures down to sub-micrometer scale. In addition, ORNL provided the specialized specimen preparation required for these techniques.

Technical information for the CRADA was presented formally at a number of CRADA reviews held at either ORNL or P&W, as well as informally via telephone conferences or Internet. Care was taken to protect all proprietary or protected CRADA information. CRADA results were also presented an invited talk at United Technologies' internal UTECA conference (April 20-23, 1998). CRADA results were also formally presented at a DOE/ER LTR Program Review by the DOE Office of Planning and Analysis on October 23, 1996.

As-Prepared Superalloys

The initial focus of the project was the characterization of the as-processed microstructure and microchemistry of the alloys, including the distribution of various alloying additions and impurities. The partitioning of the alloying elements and the site occupancy of those elements present in the ordered γ' phase can strongly effect the γ/γ' microstructure. Both partitioning of an element to the γ' phase and the preferential occupancy of the aluminum site in the γ' phase will increase the volume fraction of that phase. The partitioning of the major alloying elements to γ and γ' phases were determined by conventional APFIM and transmission AEM. The γ/γ' composition enrichment factor (which reflects the partitioning tendency to the γ phase) increased in the order of Ta, Al, Ni, W, Cr, Co, Mo, Re with only the first three elements partitioning to the γ' phase. Whereas W exhibited significant solubility in the γ' phase (especially near the γ/γ' interface), Re was strongly rejected from the γ' phase.

Though the composition of the γ and γ' phases were similar in the different as-prepared materials, there were differences in the measured composition profiles (especially near γ/γ' interfaces). In those materials, both AEM and APFIM indicated non-equilibrium Re profiles in the

thin γ phase matrix separating the large, cuboidal (primary) γ' phase. Re was enriched in the γ phase near the γ/γ' interface relative to the center of the γ phase. These local Re maxima were attributed to the strong rejection of Re during the formation and growth of γ' and slow diffusion of Re at those temperatures. In addition, AEM indicated local maxima of Co and W in the γ phase near (within 10 nm) of γ'/γ interfaces; APFIM indicated similar W local maxima as well as clustering of W in the γ phase. Both APFIM and AEM indicated the presence of fine (<20 nm), secondary γ' in the γ matrix of some of the as-prepared materials. APFIM showed that the composition of the secondary γ' was similar to that of the primary γ' particles. Atom probe tomography demonstrated the elemental distribution near such secondary γ' particles and indicated slightly different enrichment factors relative to the γ matrix than measured for the primary γ' phase.

The distribution of minor alloying additions and impurity elements such as sulfur and carbon were investigated in the as-prepared materials with all three analytical techniques. No statistically significant amounts of these elements were detected in either the γ or γ' phases by AEM or conventional APFIM. However, as a result of the larger specimen volume examined, scanning AEM of bulk specimens identified several additional phases present at low volume fraction in certain of the as-prepared materials. These phases included a Ni-Y eutectic structure (≤ 30 μm), a Ta-rich carbide, an elongated Hf-rich carbide and a Y-enriched sulfide, as well as large (≤ 10 μm) eutectic γ' . The Ni-Y eutectic structure contained a Ni-Y phase and a Ni-Al phase that was presumed to be γ' phase, as well as isolated <0.3 μm HfC particles. The formation of the Y-enriched sulfide would reduce the sulfur available in the matrix for segregation to the oxide-metal, resulting in better adherent oxide scales.

The high collection efficiency of the 3-D atom probe was employed to provide improved detection limits for minor alloying elements in the major phases and indicated that the Y was significantly depleted from the bulk composition in both γ and γ' phases. In addition, the 3-D atom probe indicated that Y was distributed inhomogeneously on a scale significantly larger than the precipitate structure in some of the modified alloys.

Convergent beam electron diffraction (CBED) of the lattice mismatch between the γ and γ' phases did not indicate any significant difference in mismatch between the various modifications of the basic superalloy composition. This result is not surprising in light of the facts that the levels of the minor alloying additions are low (<1 wt%) and that the majority of these elements are not in solution in the metal matrix, but concentrated in tertiary phases. The low solubility of these elements in either the γ or γ' phases was demonstrated by both APFIM and WDS in the scanning AEM. CBED of the γ phase indicated a slight tetragonal distortion of the matrix lattice, especially near the γ/γ' interface. Such a distortion probably arises from the lattice mismatch of the two phases and has been reported in other superalloys. However, the non-equilibrium composition profiles observed near these interfaces may also contribute to this distortion.

Oxidized Materials

The microstructural and microchemical characterization of the oxidized materials included the native oxide formed on the as-prepared materials and the oxide scales and near-scale metallic matrix in both furnace and burner rig cyclically oxidized materials. The modified alloys all exhibited dramatic improvements in weight loss during cyclic oxidation testing. Primarily scanning and transmission AEM were employed, as a result of the difficulty of preparation and analysis of such non-conducting, multilayer materials in the APFIM. Both bulk and cross-sectional specimens of the oxidized materials were examined by scanning AEM; whereas primarily cross-sectional specimens were examined by transmission AEM.

SEM examination of the external surface of a furnace-oxidized control blade indicated that the majority of the external oxide was a (Ni,Al,Cr) spinel; whereas a Cr-containing alumina was the external oxide observed near the edges of the blade. Cross-sectional SEM of the near-surface microstructure indicated a ~2 micron thick aluminum-depleted matrix zone adjacent to the oxide. The sub-micrometer scale γ/γ' structure observed in the bulk of the material was not observed in this depleted zone. A much coarser (1-2 μm) structure was observed in the depleted zone. All regions of the depleted zone showed Al levels below that of γ' . These observations indicate that the depleted zone contained only γ phase as the dominant phase present. In some oxidized materials, the Al-depleted matrix zone exhibited a single layer of columnar γ grains with grain boundaries perpendicular to the oxidized surface. This structure indicates grain growth or recrystallization of the γ phase in the Al-depleted zone and appeared to be associated with a mechanical pretreatment of the surface prior to oxidation.

Both cross-sectional SEM and TEM of the oxide scale indicated a complex, multi-phase microstructure. An external (Ni,Cr,Al) spinel layer generally adhered to the inner alumina layer, though some spalling of the spinel was observed. For alloys with rare earth additions, the alumina was continuous; whereas the alumina layer was not continuous in alloys not containing rare earth additions. Part of this discontinuous nature was associated with spalling of the entire oxide scale. In addition, hafnia particles tended to be found at the metal-alumina interface or in the alumina layer; whereas tantalum oxides particles tended to form at the alumina-spinel interface or in the spinel layer.

Localized spalling of the oxide occurred for several of the alloys which sometimes revealed the underlying metal surface. The edges of such spalled areas exhibited the transition from the external spinel scale to the internal alumina scale to the underlying metal. In certain oxidized alloys, the exposed metal surface exhibited multi-phase oxide particles extending into the metal surface. The rim of these particles was comprised of alumina and their core was either hafnium or tantalum oxides. Cross-sections of such alloys often indicated elongated oxide particles that extended 1-2 μm into the underlying metal. It is possible that the elongated Hf-rich carbides observed in the as-prepared material preferentially oxidized near the metal-oxide interface. This internal oxidation resulted in the formation of the alumina rim around the hafnium oxide core and provided mechanical interlocking of the oxide scale.

The cyclic oxidation above 1150°C resulted in coarsening of the primary γ' phase to diameters $>1\text{ }\mu\text{m}$ with some indication of precipitate rafting. A trimodal distribution of γ' precipitates was observed with the secondary and/or tertiary precipitates possibly forming during the low temperature portion of the exposure or during the final cool down after the oxidation.

Processing of these materials prior to oxidation resulted in surface-modified zones with microstructures significantly different than the underlying superalloy. The scale of the structure was generally coarser than that of the bulk superalloy and in some cases had different dominant phases or composition. These differences would impact subsequent formation of the oxide scale and possible the adherence of such modified scales.

The elemental distribution of the alloying elements in the superalloy was measured in several post-oxidation tested materials by atom probe tomography. The partitioning the alloying elements between the γ and γ' phases was found to follow the same trends as for the base alloys and thermodynamic predictions. A significant depletion in the Y content in both the γ and γ' phases was found compared to the bulk composition.

Inventions

None made or reported under this CRADA.

Commercialization

The knowledge base developed under this CRADA have and will be applied in both the current and future superalloys being developed by Pratt and Whitney. Advanced alloy compositions and processing will contribute to turbines with higher performance and better fuel efficiency.

Plans for Future Collaborations

There have been several discussions of follow-on collaborations between Pratt and Whitney and ORNL on advanced coatings and superalloy processing for improved oxidation and creep performance.

Conclusions

As a result of the complex alloy compositions and microstructures of current generations of superalloys and their oxide scales, high spatial resolution microstructural and microchemical characterization is required to understand their oxidation and creep performance under the high stress and temperature conditions experienced in a gas turbine. The distribution of both major and minor

alloy constituents can have significant impact of the alloy's behavior to such extreme conditions. This CRADA combined the experience base and industrial knowledge of Pratt and Whitney with the outstanding microcharacterization facilities and expertise at ORNL. The characterization of the structural and microchemical changes that occur under exposure to high temperature, as well as oxidizing conditions has contributed to understanding the impact of alloy chemistry and processing on the performance of the current generation of superalloys under development. Based on this understanding, materials with improved performance and possibly lower cost will be developed.

DISTRIBUTION

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