Nickel Based Superalloy with Improved Weldability and Oxidation Resistance

Fifth Quarterly Report for the Period November 1999 to January 2000

Submitted by:
George Simkovich
Eric Whitney

The Pennsylvania State University
University Park, PA 16802

February 29, 1999⁰⁰ [sic]
2000

Prepared for:
Mr. David Crouch, EE-24
United States Department of Energy
1000 Independence Avenue, SW
Washington D.C., 20585
Under Grant Number - DE-FG36-98GO10316

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Table of Contents

List of Tables.....	iv
List of Figures	v
Summary	1
Project Aim	1
Project Objective	1
Summary of Project Work Plan.....	1
Task 1 - Commercial Interface	1
Task 2 - Evaluation of Test Alloy Composition.....	1
Task 3 - Follow-on Alloy Definition.....	2
Task 4 - Development of Preliminary Full Scale Qualification Program	2
Task 5 - Reporting.....	2
Description of Progress	2
Task 1	2
Task 2	2
1000 °C Oxidation Test Results for Ni-Al and Ni-Al-Pd Alloys.....	3
1000 °C Oxidation Test Results for Ni-Cr and Ni-Cr-Pd Alloys.....	5
1000 °C Oxidation Test Results for Ni-Al-Cr ternary and Ni-Cr-Al-Pd quaternary Alloys	6
Comparison of all Pd-bearing alloys under current investigation	8
Comparison Current Test Alloys with Previous Test Alloys 1, 2, 2 NoPd, and 3	9
Accomplishments	10
Task 1	10
Task 2	10
Task 3	11
Task 4	11

Task 5	11
Future Activities	11
Task 1	11
Task 2	11
Task 3	11
Task 4	11
Task 5	11
Changes in Key Personnel	11
Appendix	12
References	14

List of Tables

Table I Experimental Ni-Pd-X Compositions	3
Table II 1000°C Parabolic Rate Constants for Ni-Al-Pd Alloys.....	5
Table III 1000°C Parabolic Rate Constants for Ni-Cr-Pd Alloys	6
Table IV 1000°C Parabolic Rate Constants for Ni-Cr-Al-Pd and Ni-Cr-Al-Pd Alloys....	7
Table V 1000°C Parabolic Rate Constants for Some Current Alloys and Alloys 1, 2, 2 NoPd, and 3	10
Table VI Experimental Compositions Previously Investigated	12

List of Figures

Figure 1 1000°C Isothermal Oxidation of Ni-Al and Ni-Al-Pd Test Alloys	4
Figure 2 1000°C Isothermal Oxidation of Alloys 10Al and 5Al 0Pd	4
Figure 3 1000°C Isothermal Oxidation of Ni-Cr and Ni-Cr-Pd Test Alloys	6
Figure 4 1000 °C Oxidation Test Results for Ni-Al-Cr ternary and Ni-Cr-Al-Pd quaternary Alloys	7
Figure 5 1000°C Isothermal Oxidation, Al-Cr-Pd Alloy Test Data	8
Figure 6 1000°C Isothermal Oxidation, 0-3000 Minutes	9
Figure 7 Comparison of Current Alloys with Previously Tested Alloys.....	10
Figure 8 1000°C Isothermal Oxidation of Alloys 1, 2, 2 NoPd, and 3	13
Figure 9 1200°C Isothermal Oxidation of Alloys 1, 2, 2 NoPd, and 3	13

Summary

This program is part of the U.S. Department of Energy (DoE) Energy Related Inventions Program (ERIP). The purpose of ERIP is to promote and facilitate the development of energy saving technologies that may not otherwise be developed solely by commercial enterprises. The program has been highly successful in achieving its mission.

Project Aim

The aim of this project is to determine and provide technical and economic data to a commercial end user of the alloy so that a full-scale alloy qualification program can be defined and implemented. The object of this project is to define the compositional range for a new alloy that is suitable for evaluation and qualification by a commercial enterprise. Alloy properties that will need to be determined include weldability, oxidation resistance, creep strength, resistance to thermo-mechanical fatigue, microstructure stability, and cost. Test results will be used to finalize the compositional range of an alloy that will undergo a rigorous qualification process.

Project Objective

There are 4 objectives:

1. Define a compositional range for a new alloy that is suitable for evaluation by a commercial enterprise.
2. Optimize alloy properties of weldability and oxidation resistance, creep strength, thermo-mechanical fatigue, microstructure stability, and cost.
3. Evaluate experimental materials in a real manufacturing environment.
4. Develop a range of alloy compositions for final qualification process.

Summary of Project Work Plan

Task 1 - Commercial Interface

In this task, the principal investigators will cultivate and maintain a technical and business relationship with an industrial end-user. This is a critical step to the development of an alloy ready for a rigorous qualification program. Continual involvement of an industrial partner will minimize risk and increase the possibility of a successful program.

Task 2 - Evaluation of Test Alloy Composition

This is the most technical part of the program. The relationship between palladium, chromium, and aluminum and alloy properties will be investigated, most notably in terms

of weldability and oxidation resistance. This task includes determining alloy compositions, obtaining alloy powders, testing, and evaluation.

Task 3 - Follow-on Alloy Definition

Two compositions will be evaluated based upon the belief that they will be suitable for a follow-on qualification program. By consulting with an industrial end-user, the compositions will be defined and designed to maximize cost/performance of the alloys. Additional alloy powders will be obtained. Follow-on compositions will undergo a series of tests with key input from an industrial end-user. Test results may be used as part of a full-scale alloy development program.

Task 4 - Development of Preliminary Full Scale Qualification Program

The industrial end-user and the principal investigators will develop a preliminary plan for full-scale qualification. The plan will address the issues necessary to obtain Federal Aviation Administration approval for use as a repair material for turbine blade tips.

Task 5 - Reporting

Reporting will be the primary method of transmitting and archiving final technical data, results, conclusions,

Description of Progress

Progress description will be detailed by Task.

Task 1

Efforts to maintain working relationship with Sermatech continued during this quarter. Revised intellectual property agreements were transmitted to Sermatech for review. A trip to Sermatech was postponed so that additional oxidation data could be generated.

The University received a PTO action on its application. All claims were disallowed. However, the patent examiner report detailing the office action indicated that the cited prior art 'fails to meet all the limitations of the instant invention'. This statement provides insight into how the prior art can be overcome. The University has retained outside patent counsel to continue the prosecution of the patent and will be preparing a response. The response is due November 12, 1999. This will be reported on in the next quarterly report.1

Task 2

Based on the review of prior work and the needs of this program a series of experimental alloys have been established and shown in Table I. Note: oxidation test results for alloys tested prior to the start of this program are given in the Appendix, reference to this data

may be helpful in understanding the current results. As can be seen the Cr level is varied from 5 to 20 atomic percent in the Ni-Pd-Cr alloys and Al is varied from 5 to 10 atomic percent in the Ni-Pd-Al alloys. Testing these ternaries will help us separate the effects of Pd on Cr_2O_3 and Al_2O_3 formation. This information will be used to help adjust the level of Cr and Al in a commercial alloy. Finally, the last two alloys are chosen to test the effect of Pd on ternary to quaternary alloys. Other solute constituents, such as Co, Mo, and others do not complicate the analysis. During subsequent analysis it was concluded that several non-Pd bearing alloys should also be included into the experimental matrix, to help establish the effect of Pd on oxidation at low and high temperatures.

Table I Experimental Ni-Pd-X Compositions

Alloy I.D.	Atomic Percent			
	Ni	Pd	Cr	Al
5Cr-5Pd	90	5	5	-
10Cr-5Pd	85	5	10	-
20Cr-5Pd	75	5	20	-
5Al-5Pd	90	5	-	5
7Al-5Pd	87.5	5	-	7.5
10Al-5Pd	75	5	-	10
15Cr-5Al-5Pd	75	5	15	5
15Cr-10Al-Pd	80	5	15	10
5Cr 0Pd	95	0	5	-
20Cr 0Pd	80	0	20	-
5Al 0Pd	95		-	5
10Al 0Pd	90		-	10
15Cr5Al 0Pd	80		15	5
15Cr10Al 0Pd	75		15	10

1000°C Oxidation Test Results for Ni-Al and Ni-Al-Pd Alloys

Figure 1 shows the test results for the Ni-Al-Pd alloys at 1000°C. The results for 10Al and 5Al 0Pd are almost coincident and cannot be resolved in the figure, the test results for these two alloys are shown in Figure 2. The test data for Alloy10Al extends to only 278 minutes. The parabolic rate constant for each alloy was also calculated and is shown in Table II.

Figure 1 1000°C Isothermal Oxidation of Ni-Al and Ni-Al-Pd Test Alloys

Figure 2 1000°C Isothermal Oxidation of Alloys 10Al and 5Al 0Pd

Table II 1000°C Parabolic Rate Constants for Ni-Al-Pd Alloys

Alloy I.D.	Parabolic Rate Constant ($\text{mg}^2/\text{cm}^4 \text{ min}$)
5Al-5Pd	6.477E-02
5Al-0Pd	2.217E-02
7Al-5Pd	2.946E-02
10Al-5Pd	1.585E-02
10Al-0Pd	3.509E-02

From Figure 1, Figure 2, and Table II the following observations can be made:

- In the presence of 5% Pd, increasing Al content from 5% to 10% decreases mass gain with time and also decreased the parabolic rate constant. There is a 4X difference in the parabolic rate constant between alloy 5Al and 10Al
- At 5% Al, 5% Pd increases mass gain with time and also increases the parabolic rate constant by about 3X.
- At 10% Al, 5% Pd decreased mass gain with time and also decreased the parabolic rate constant by about 2.2X
- Of the alloys, alloy 10Al and 5Al 0Pd performed best. Alloy 10Al had a slightly lower parabolic rate constant
- The data is inconsistent with the more complex alloys (Alloy 1, 2, 2 NoPd, and 3) in that the presence of 5% Pd in the 10%Al alloy showed a decrease in oxidation mass gain over the Ni-10%Al binary. In the more complex alloys Pd always increased oxidation mass gain, at 1000°C

1000°C Oxidation Test Results for Ni-Cr and Ni-Cr-Pd Alloys

Figure 3 shows the test data for the Ni-Cr and Ni-Cr-Pd alloys. As expected, oxidation resistance increases with increasing Cr level. The addition of 5% Pd decreased oxidation resistance for alloys that contain 5 and 20% Cr. This data is consistent with the more complex alloys previously tested. Table III lists the corresponding parabolic rate constants.

Figure 3 1000°C Isothermal Oxidation of Ni-Cr and Ni-Cr-Pd Test Alloys

Table III 1000°C Parabolic Rate Constants for Ni-Cr-Pd Alloys

Alloy I.D.	Parabolic Rate Constant ($\text{mg}^2/\text{cm}^4\text{min}$)
5Cr-5Pd	1.7910E-01
10Cr-5Pd	8.7730E-02
5Cr-0Pd	5.9240E-02
20Cr-5Pd	1.2800E-03
20Cr-0Pd	4.6280E-04

The following observations can be made:

- As expected, increasing Cr content decreased oxidation rate and total mass gain
- The addition of 5% Pd to 5 and 20% Cr alloys increased oxidation rate over alloys that did not contain Pd
- The behavior of the tested Ni-Cr binary and Ni-Cr-Pd ternary alloys is consistent with the more complex alloys, Alloys 1, 2, 2 NoPd, and 3.

1000°C Oxidation Test Results for Ni-Al-Cr ternary and Ni-Cr-Al-Pd quaternary Alloys

The use of binary and ternary alloys is useful, but the alloy that will be developed in this program will be more complex. To consider this, two ternary and two quaternary alloys were fabricated and tested. Based on previous work and numerous data contained in literature, a Cr level of 15% appears to be the minimum necessary to achieve good low temperature oxidation resistance when Al levels must remain as low as possible. In these

tests, the chromium level was fixed at 15% and the Al level varied between 5 and 10%. Pd was varied between 0 and 5%. The isothermal oxidation results are shown in Figure 5. The results are very interesting and encouraging. Note that the presence of Pd decreased the overall mass change over the corresponding Pd-free alloy. These results are in contrast to previous work on more complex alloys. Also interesting are the results of the 5% Al alloys. For the Ni-5Al binary the addition of Pd increased oxidation, as shown in Figure 1. But, in the presence of 15% Cr Pd decreased oxidation. This is a significant observation.

Figure 4 1000 °C Oxidation Test Results for Ni-Al-Cr ternary and Ni-Cr-Al-Pd quaternary Alloys

The parabolic rate constants for the Ni-Al-Cr ternary and Ni-Cr-Al-Pd quaternary alloys are shown in Table IV. The parabolic rate constants for the 5% Al alloys is less than for the 10% alloys. This is interesting and may indicate a difference in the defect structure of the oxide scale between the two alloys. The parabolic rate constant for the 15Cr-10Al-0Pd is 6X higher than it is for the 5Cr-5Al-5Pd alloy. The parabolic rate constant for 15Cr-5Al-0Pd is 2.8 times higher than it is for 15Cr-5Al-5Pd.

Table IV 1000°C Parabolic Rate Constants for Ni-Cr-Al-Pd and Ni-Cr-Al-Pd Alloys

Alloy I.D.	Parabolic Rate Constant ($\text{mg}^2/\text{cm}^4\text{min}$)
15Cr-5Al-0Pd	2.71E-04
15Cr-5Al-5Pd	9.78E-05
15Cr-10Al-0Pd	5.83E-04
15Cr-10Al-5Pd	2.89E-04

The following observations can be made:

- The addition of Pd to ternary 15Cr-Al alloys decreased the oxidation and parabolic rate constants of the test alloys. These results are unlike the previous results for more complex alloys.

Comparison of all Pd-bearing alloys under current investigation

Figure 5 and Figure 6 show the isothermal oxidation test results for all the Pd-bearing alloys tested under the current program. Of the alloys tested the quaternary alloys 15Cr-5Al-5Pd and 15Cr-10Al-5Pd showed the lowest oxidation mass change, and also the lowest parabolic rate constants.

Figure 5 1000°C Isothermal Oxidation, Al-Cr-Pd Alloy Test Data

Figure 6 1000°C Isothermal Oxidation, 0-3000 Minutes

Comparison Current Test Alloys with Previous Test Alloys 1, 2, 2 NoPd, and 3

Figure 7 shows the oxidation test results for some of the current alloys and for Alloys 1, 2, 2 NoPd, and 3. As shown in the Appendix, alloys 1, 2, 2 NoPd, and 3 showed oxidation behavior similar to earlier work on Alloy 738 modified with palladium. That is the Pd-bearing alloys all showed higher mass gain and higher parabolic rate constants than alloys that do not contain palladium. Table V shows the corresponding parabolic rate constants for the alloys in Figure 7.

The results are interesting in that the present alloys that contain Pd are equal to or better than Alloys 1, 2, and 3. And that alloy 15Cr-5Al-5Pd is essentially similar to Alloy 2 No Pd. As noted in the Appendix, the composition of Alloys 1, 2, and 3 contain 12%Pd. Further, the Pd level in the present alloys is the lowest yet tested. Therefore, it may be that a threshold value exists for Pd level in these alloys, above which 1000°C isothermal oxidation resistance is lowered. If this is the case, then the threshold value must be tested at 1200°C to determine if this level of Pd is sufficient to impart improved oxidation resistance at higher temperatures.

Figure 7 Comparison of Current Alloys with Previously Tested Alloys

Table V 1000°C Parabolic Rate Constants for Some Current Alloys and Alloys 1, 2, 2 NoPd, and 3

Alloy I.D.	Parabolic Rate Constant ($\text{mg}^2/\text{cm}^4 \text{min}$)
20Cr-5Pd	1.280E-03
15Cr-5Al-5Pd	9.780E-05
15Cr-10Al-5Pd	2.885E-04
Alloy 1	9.245E-04
Alloy 2	3.992E-04
Alloy 2 NoPd	1.169E-04
Alloy 3	7.256E-04

Accomplishments

Task 1

- Continued to develop relationship with Sermatech

Task 2

The following accomplishments were made in Task 2:

- Completed oxidation testing at 1000°C
- Testing started at 1200°C
- Detailed evaluation of 1000°C data underway

- Results show that 1000°C oxidation of test alloys to be superior to previous alloys

Task 3

No activity on this task.

Task 4

No activity on this task.

Task 5

Reporting is current with program milestones.

Future Activities

Task 1

Continued effort to establish an IP agreement will be made with Sermatech. The investigators will assist outside patent counsel in the preparation of a response to the PTO action received during this past reporting period.

Task 2

Complete 1200°C isothermal oxidation testing. Begin metallurgical evaluation of tested samples to determine extend of internal oxidation.

Task 3

Establish preliminary composition for test in this Task.

Task 4

No activity is planned on this task.

Task 5

Sixth quarter report will be prepared, no papers or presentations are anticipated.

Changes in Key Personnel

None.

Appendix

Previous oxidation studies on Pd-bearing alloy have been conducted at Penn State. The initial work [1] was performed on a modified Alloy 738. This work showed that Pd was effective in decreasing high temperature oxidation rate. At low temperatures it was theorized that Pd increased oxidation rate by increasing oxygen diffusion into the alloy or by decreasing Al or Cr diffusion outward to the metal-scale interface. Subsequent work [2] on a modified Alloy 625 (which is essentially an Al-free alloy) showed that Pd is not as effective in decreasing high temperature oxidation rate in the absence of aluminum. Work performed at Penn State on a series of experimental alloys verified the effect of Pd on the high and low temperature oxidation rate. Table VI shows the composition of the previously studied alloys, Alloys 1, 2, 2 NoPd, and 3. Note that these alloys contain other solutes, specifically Co, Mo, and Nb. These elements are typically added to superalloys to enhance strength [3]. Co is added to improve creep resistance. Mo and Nb are typically added as solid solution strengtheners, Mo strengthens the γ matrix and Nb strengthens the γ' phase. These elements were added to Alloy 1, 2, 2 NoPd, and 3 to for these reasons. The compositions of Alloy 1, 2, 2 NoPd, and 3 are listed in Table VI.

Table VI Experimental Compositions Previously Investigated

Experimental Alloys 1, 2, 2 NoPd, and 3 Composition, atomic percent				
Element	Alloy 1	Alloy 2	Alloy 2 NoPd	Alloy 3
Al	5	7	7	9
Co	10	10	10	10
Cr	18	18	18	18
Mo	6	6	6	6
Nb	1	1	1	1
Ni	48	46	58	44
Pd	12	12	0	12

The oxidation data for Alloys 1, 2, 2 NoPd, and 3 are given in Figure 8 and Figure 9. Note the reversal of rankings (lower mass change being better) between the 1000° and 1200° data. Alloy 2 NoPd was far better than the other alloys at 1000°C but at 1200°C Alloy 2 NoPd was unquestionably worse than the Pd-bearing compositions. The difference in oxidation behavior between Alloy 2 and Alloy 2NoPd is solely due to the presence of Pd. The goal of the present task is to determine if a Pd –bearing composition can be derived that results in improved oxidation resistance at low and high temperatures.

Figure 8 1000°C Isothermal Oxidation of Alloys 1, 2, 2 NoPd, and 3

Figure 9 1200°C Isothermal Oxidation of Alloys 1, 2, 2 NoPd, and 3

It is useful to compare the data for the current series of alloys to Alloys 1, 2, 2 NoPd, and 3. The comparison can be made in terms of alloys ranking in a group and time dependent mass gain. Ranking the alloys in terms of the parabolic rate constant can also show important difference between alloys.

References

1. Whitney, E., *Isothermal Oxidation of a Palladium Modified Superalloy, Alloy 738*, in *Metals Science and Engineering*. 1995, The Pennsylvania State University: University Park. p. 120.
2. Whitney, E., G. Simkovich, and J. Fink. *High Temperature Oxidation of a Modified Alloy 625*. in *Superalloys 718,625,706 and Various Derivatives*. 1997. Pittsburgh, PA, USA: The Minerals, Metals, and Materials Society.
3. Decker, R.F. and C.T. Sims, *The Superalloys*, ed. C.T. Sims and W.C. Hagel. 1972: John Wiley & Sons.

Distribution

A.

Reports Control Center
U.S. Department of Energy
Golden Field Office
1617 Cole Blvd.
Golden, CO 80401-3393

B.

Mr. David Crouch
EE-24
U.S. Department of Energy
1000 Independence Avenue, S.W.
Washington D.C., 20585

C.

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 72
Oak Ridge, TN 37830
(final report only)

Mr. John Helm

Director
Thermal Spray Technology
Sermatech Technical Services
155 South Limerick, PA 19468
(Technical Report)