

FINAL REPORT
DE-FG02-03ER46035
Georgia Tech Research Corporation
“Resistivity-Microstructure Relationships in Nickel Base Superalloys
Used in Gas Turbine Engines for Power Generation
and as Interconnects in Solid Oxide Fuel Cells”
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Highlights of Accomplishments:

- A total of (24) papers have been submitted and/or published since the beginning of this 3-year grant(none of the papers published during the previous grant from 2003-2007 are listed). In addition, there are several other manuscripts currently under preparation.
- Several of the papers report on analytical derivations, finite element simulations, microstructural development and small angle scattering experiments in Waspaloy nickel base superalloys as well as neutron reflectometry of other materials.
- The most important new contribution for this grant was the development of a microstructural model, based on analysis of the small angle scattering spectra that can relate the measured resistivity to the precipitate population present in precipitation hardened alloys, and in particular for Waspaloy, a nickel base superalloy.
- The list of papers also include reports of some of the activities carried out while the P.I. was on sabbatical at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory during the 2007-2008 academic year and their continuation.
- USAXS experiments were carried out at the APS in September 2007 and March 2008. The results from the September runs were reported at the DOE Contractors Meeting in October 2007. We also presented research posters at the APS users workshop in May 2007, May 2008 and May 2009. Some of the USAXS results were also presented at the MS&T conference in Pittsburgh in October 2009 and the MRS Spring Meeting in San Francisco in April 2010.
- We also acquired SANS data at the HFIR facility on five separate occasions (April 2008, July 2008, January 2009, December 2009 and January 2011). The main advantage of using SANS is that much thicker specimens can be evaluated and thus sample preparation is less onerous than for the extremely thin USAXS specimens required. During the December 2009 run, we carried out the first in-situ precipitation hardening run. We presented a paper at the International Conference on Neutron Scattering held in Knoxville, TN in May 2009 and also presented the SANS results at the International Conference on Superalloys in Pittsburgh in October 2010. As a result of that conference, we were invited to give an invited talk at the THERMEC Conference held in Montreal in August 2011. Some of the SANS results were also presented at the Spring 2010 MRS meeting described earlier.
- Two graduate students were fully funded by this grant. V. Siva Kumar G. Kelekanjeri, who graduated with his PhD in 2007 and stayed on as a post-doc for a year.

The second student that was fully funded was Ricky L. Whelchel, who started out as an undergraduate researcher in 2006 and graduated with a M.S. in August 2011. He was awarded Best Presentation at the International Bodycote Competition in Manchester, England in April 2008. The award winning paper appeared in the *International Heat Treating and Surface Journal* in 2009. More recently, Prof. Gerhardt and Mr. Whelchel were awarded an American Society for Non-destructive Testing Fellowship (ASNT), which is being used to conduct the last set of experiments that will be published.

- A paper reporting the usage of the AFM to characterize the microstructure of superalloys was published in the MRS online proceedings for Fall 2007.
- During the 2008-2009 academic year, a second Ph.D. student, Will Gibson, was hired in order to begin evaluating metallic alloys used in fuel cell interconnects. At that time we tried to establish a collaboration with the Fuel Cell group at Pacific Northwest National Laboratory. Unfortunately, the student had a change of heart and decided to leave graduate school in May 2009.
- Several other graduate students benefitted from this grant (Chunqing Peng, Salil Joshi and Rachel Muhlbauer). The first two were fully funded by the Institute for Paper Science and Technology at Georgia Tech but their work benefitted from the Scanning Probe Microscope and the neutron scattering and neutron reflectometry work that was initiated while the PI was on sabbatical at Oak Ridge National Labs during the 2007-2008 academic year. Rachel Muhlbauer started her PhD in August 2010 and is now being funded via an NSF-IGERT scholarship. Four papers have already been published by this group of students and there are more in preparation.

Sabbatical related activities

- The principal investigator spent her sabbatical year (June 2007-June 2008) at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory funded in part by CNMS, this DOE grant, Georgia Tech and her other research grants. She worked primarily with the Nanophysics group learning more hands-on techniques with the AFM and helping the CNMS establish two impedance spectroscopy based facilities:
 - She helped order and install an impedance spectroscopy facility to study solar cell type materials and other materials that can undergo changes upon exposure to different wavelengths of light. She is currently working with several members of the Functional Nanomaterials group on carbon nanotube based devices and other materials and it is anticipated that several publications will be forthcoming.
 - She is currently finalizing the software needed to interface impedance analyzers with scanning probe microscopes so that impedance spectra can be acquired in a data array fashion. This has been possible because the nanophysics group had already been able to accomplish this task for PiezoForce Microscopy (referred to as SS-PFM). Nevertheless, the PI's background in impedance spectroscopy has been instrumental in making this project a reality. At least two papers are expected to be outcomes of this activity.
 - Both of these facilities will be unique around the world and many users have already shown substantial interest in being able to use them.
 - At the same time, the PI has benefited tremendously from being at ORNL and has started several other collaborations:

- Characterization of some high surface area metallorganic terephthalates (a paper based on this work was published in 2009).
- Development of standards for accurate electrical properties characterization using AFM/SPMs. Thermally oxidized films were patterned on silicon wafers and electrode patterning and sizes were developed so that stray capacitance determination could be standardized in the future. This project is continuing. In order to assist with the standard characterization, a post-doc was hired to assist with some finite element simulation that could predict the expected properties as a function of frequency. Tremendous progress was made during the short time that Dr. Surajit Kumar worked on this project and several manuscripts have been drafted but have not yet been published. Dr. Kumar is no longer working in Prof. Gerhardt's group as he was able to secure an industrial position.
- Neutron reflectometry measurements were initiated in November 2009 at the SNS in collaboration with Dr. Valeria Lauter. We are looking at the structure of layer by layer assembled ITO thin films. The first paper on this technique was published in 2011. More papers are in preparation and will be used as the starting point for a future DOE BES research grant.

Publications acknowledging this research grant:

1. V.S.K.G. Kelekanjeri and R.A. Gerhardt, "Electric field distribution within a metallic cylindrical specimen for the case of an ideal two-probe impedance measurement" *J. Applied Physics* 101, 044904 (2007).
2. V. Siva Kumar G. Kelekanjeri and Rosario A. Gerhardt, "Microstructure – Resistivity Correlations in Solution treated and Aged Waspaloy Microstructures," *Materials Research Society Fall 2006 Online Proceedings*, 0977E (2007).
3. V.S.K.G. Kelekanjeri and R.A. Gerhardt, "Analytical Derivation of Geometrical Correction Factors for Four-probe dc Measurements on a Cylindrical Specimen" *Measurement Science and Technology* 19, 025701(2008).
4. V.S.K.G. Kelekanjeri and R.A. Gerhardt, "Computation of the Complex Impedance of a Cylindrical Conductor in an Ideal Two-Probe Configuration," invited chapter for a book entitled Recent Advances in Modeling and Simulation (ed. G. Petrone and G. Cammarata) pp. 85-110(2008). I-Tech Education and Publishing (ISBN 978-3-902613-25-7).
5. V.S.K.G. Kelekanjeri and R.A. Gerhardt, "SPM Based Electrical Characterization of Aged Waspaloy Microstructures," 2007 MRS Fall Meeting Proceedings, volume 1025E, Boston, MA, USA, 2007
6. V.S.K.G. Kelekanjeri and R.A. Gerhardt, "Etch Pit and □ Precipitate Evolution in Controlled Waspaloy Microstructures Aged at 725°C, 800°C and 875°C," *Acta Materialia* 57[2]616–627(2009).
7. Ricky L. Wheelchel, V. Siva Kumar G. Kelekanjeri, and Rosario A. Gerhardt, "Mechanical and Electrical Characterization in Age Hardened Waspaloy Microstructures," INVITED

paper for International Bodycote Heat Treatment Award for 2008, *International Heat Treating and Surface Engineering Journal* 3[1/2].35-39(2009).

8. V S. K.G. Kelekanjeri, L.K. Moss, R.A. Gerhardt and J. Ilavsky, "Quantitative Study of Microstructural Evolution in Aged Waspaloy Microstructures with Different Prior Homogenizing Treatments," *Acta Materialia* 57(16), 4658-4670 (2009).
9. R.L. Whelchel, V. S. K. G. Kelekanjeri, Rosario A. Gerhardt, Jan Ilavsky, and Ken C. Littrell, "Correlating Small Angle Scattering Spectra to Electrical Resistivity Changes in a Nickel-Base Superalloy," *Materials Research Society Symposium Proceedings* (2010), vol. 1262(In-Situ and Operando Probing of Energy Materials at Multiscale Down to Single Atomic Column--Power of X-Rays, Neutrons and Electron Microscopy), No pp. given, Paper #: 1262-W10-05.
10. R. L. Whelchel, V.S.K.G. Kelekanjeri, R.A.Gerhardt and J. Ilavsky, "Correlations between Ultra Small Angle X-ray Scattering Data and Measured Resistivity in an Age-Hardened Superalloy," *Met. Mat. Trans. A* 42A, 1362-1372(2011).
11. R.L. Whelchel, Rosario A. Gerhardt, and Ken Littrell, "Structure-Property Relationships in Waspaloy via Small Angle Scattering and Electrical Resistivity Measurements," *7th International Symposium on Superalloy 718 and Derivatives Conference Proceedings*, held in Pittsburgh in October 2010. Published on CD-ROM.
12. Ricky L. Whelchel, Rosario A. Gerhardt and Ken C. Littrell, "Modeling the Electrical Response of Waspaloy due to the Nucleation, Growth, and Coarsening of γ' ," *Materials Science Forum Vols. 706-709*, 2406-2411(2012).
13. Ricky L. Whelchel et al., "Comparison of in-situ vs. ex-situ aging of nickel base superalloy Waspaloy conducted at 725 °C," to be submitted to ASNT Journal.
14. Rosario A. Gerhardt, "Non-destructive Evaluation of Materials Microstructure via Electrical and Scattering Methods," in preparation.

Publications related to sabbatical activities

15. Cantwell G. Carson, Kenneth Hardcastle, Justin Schwartz, Xiaotao Liu, Christina Hoffmann, Rosario A. Gerhardt, and Rina Tannenbaum, "Synthesis and Structure Characterization of Copper Terephthalate Metal–Organic Frameworks," *Europ. J. Inor. Chem.* (16), 2338-2343 (2009).
16. Surajit Kumar and Rosario A. Gerhardt, "Numerical Study of the Electrical Properties of Insulating Thin Films Deposited on a Conductive Substrate," *COMSOL Conference Proceedings*, Boston, November 2009.
17. Salil Joshi, Gregory Book and Rosario A. Gerhardt, "Effect of heat treatment on the electrical and optical properties of cold-sputtered indium tin oxide films," *MRS Spring Meeting Proceedings, Volume 1256E*, San Francisco, CA. 2010.
18. Matthew P. Garrett, Ilia N. Ivanov, Rosario A. Gerhardt, Alex Puretzky and David Geohegan, "Separation of junction and bundle resistance in SWNT percolation networks by impedance spectroscopy," *Applied Physics Letters* 97, 163105 (2010). *Republished in Virtual Journal of Nanotechnology*.

19. Chunqing Peng, Yonathan S. Thio and Rosario A. Gerhardt, "pH-Controlled Exponential Layer-By-Layer Growth of Polyelectrolytes/Inorganic Nanoparticles Multilayers," *Chemistry of Materials*, 23[20],4548-4556(2011).
20. Salil Joshi, Gregory W. Book and Rosario A. Gerhardt, "A Comparative Study of the Effect of Heat Treatment on the Microstructure and Properties of Colloidal ITO Thin Films and Cold-Sputtered ITO Films", *Thin Solid Films* 520, 2723-2730(2012).
21. Chunqing Peng, Yonathan S. Thio and Rosario A. Gerhardt, "Effect of Precursor-layer Surface Charge on the Layer-by-Layer Assembly of Polyelectrolyte / Nanoparticle Multilayers," *Langmuir* 28, 84–91(2012).
22. Surajit Kumar and Rosario A. Gerhardt, "Numerical study of the electrical properties of insulating thin films deposited on a conductive substrate: model development, effect of film thickness and electrode size," *Measurement Science and Technology* 23,035602 (17pp) (2012).
23. Rachel L. Muhlbauer and Rosario A. Gerhardt, "A Review on the Synthesis of Carbon Nanotube Thin Films," In: Carbon Nanotubes: Synthesis, Properties and Applications Ed. Dr. Ajay Kumar Mishra, Nova Science Publishers, Inc., in press(2012).
24. I.N. Ivanov, M.P. Garrett and R.A. Gerhardt, "Carbon Nanotube Assemblies for Transparent Conducting Electrodes," *Invited chapter* for a book, Springer Publications, in press (2012).

Project Participants:

Principal Investigator:	Rosario A. Gerhardt (GT)
Post-Doctoral Research Associates:	V. Siva Kumar G. Kelekanjeri(GT- May 2007-April 2008 – full support. Currently working at GE Global Research in Bangalore, India) Surajit Kumar (GT – June 2008-January 2009 – full support. Currently working at Applied Materials)
Graduate Students:	V. Siva Kumar G. Kelekanjeri(PhD awarded May 2007 – see above) Ricky L. Whelchel (M.S. awarded in August 2011 started May 2008 –December 2010- full support) William Gibson (started November 2008 – left in May 2009 – full support) Rachel Muhlbauer (August 2010-present – partial support)
Undergraduate Students:	Lewis K. Moss (GT – Nov. 2005-May 2008 – partial support. Currently going to medical school at Emory University) Ricky L. Whelchel(January 2006-May 2008 –partial support – see above)
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