Low Temperature Surface Carburizing of Stainless Steels

ITP Materials Project and Portfolio Review

June 2, 2005

Chicago, IL

Low Temperature Surface Carburizing of Stainless Steels (CPS# 16948)

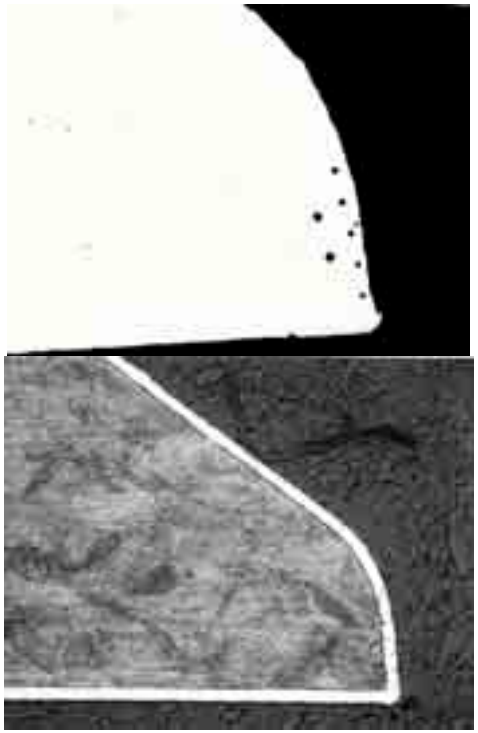
Goal: Demonstrate improvements in performance characteristics of austenitic stainless steels and components by applying a low temperature carburization process currently used for conformal surface hardening AISI 316 components

Challenge: Development of performance data to illustrate process benefits

Benefits: Substantial reduction in service-induced degradation (wear, corrosion, fatigue) of austenitic stainless steel parts, resulting in improved energy efficiencies

Potential End-User Applications: impeller pumps for the chemical and petroleum industries; steam traps; bearings and race surfaces

FY06 Activities: Finalize performance testing of selected alloys; Experimental verification of thermodynamic model; continue identification of potential customers and applications



Participants: Swagelok, Case Western Reserve University, Oak Ridge National Laboratories, Energy Industries of Ohio, Spirax Sarco

Low Temperature Surface Carburizing of Stainless Steels (CPS# 16948)

Barrier-Pathway Approach

Barriers

- Austenitic stainless steels possess excellent corrosion resistance but:
- Low surface hardness
- Poor wear resistance
- Poor frictional properties

Pathways

- Microstructural and properties characterization of treated alloys
- Thermodynamic modeling
- Component performance evaluation for economic analysis: improvements in energy efficiency

Critical Metrics

- Double the hardness of untreated material
- Uniform treatment
- No carbide precipitation
- Performance improvement (wear, corrosion, fatigue)

Benefits (est.)	2020
Energy Savings	44.7 trillion Btu
Cost Savings	$260 million
Carbon Reduction	0.89 MMTCe

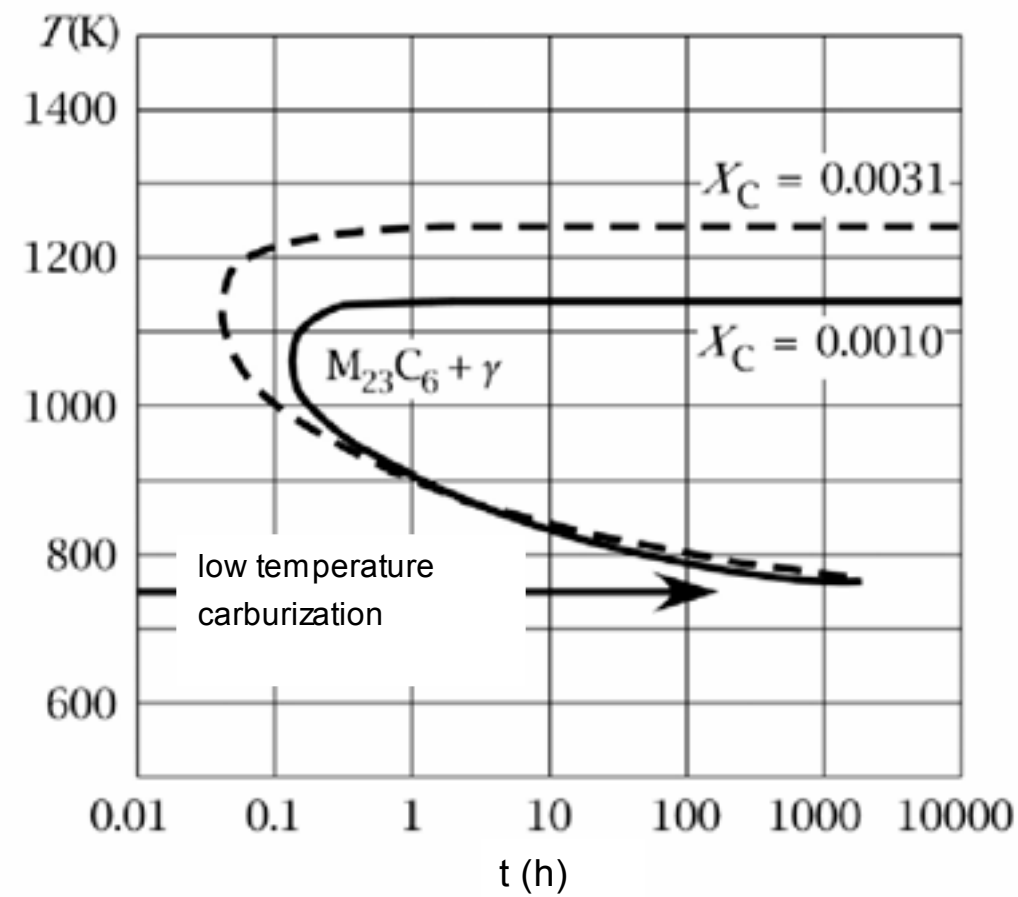
Project Tasks

1. Manufacture/procure alloys and specimens (Swagelok)
2. Processing of alloys (Swagelok)
3. Initial evaluations (Swagelok)
4. Microstructural characterization (Case)
5. Thermodynamic modeling (Case)
6. Corrosion testing: treated and untreated alloys (Swagelok, ORNL, Case)
7. Mechanical testing (Case)
8. Tribological evaluations (ORNL)
9. Component testing (EIO, ORNL, Spirax Sarco, Case, Swagelok)
10. Manufacture of experimental alloys (ORNL)
11. Meetings and reports (Swagelok)

Prior Work

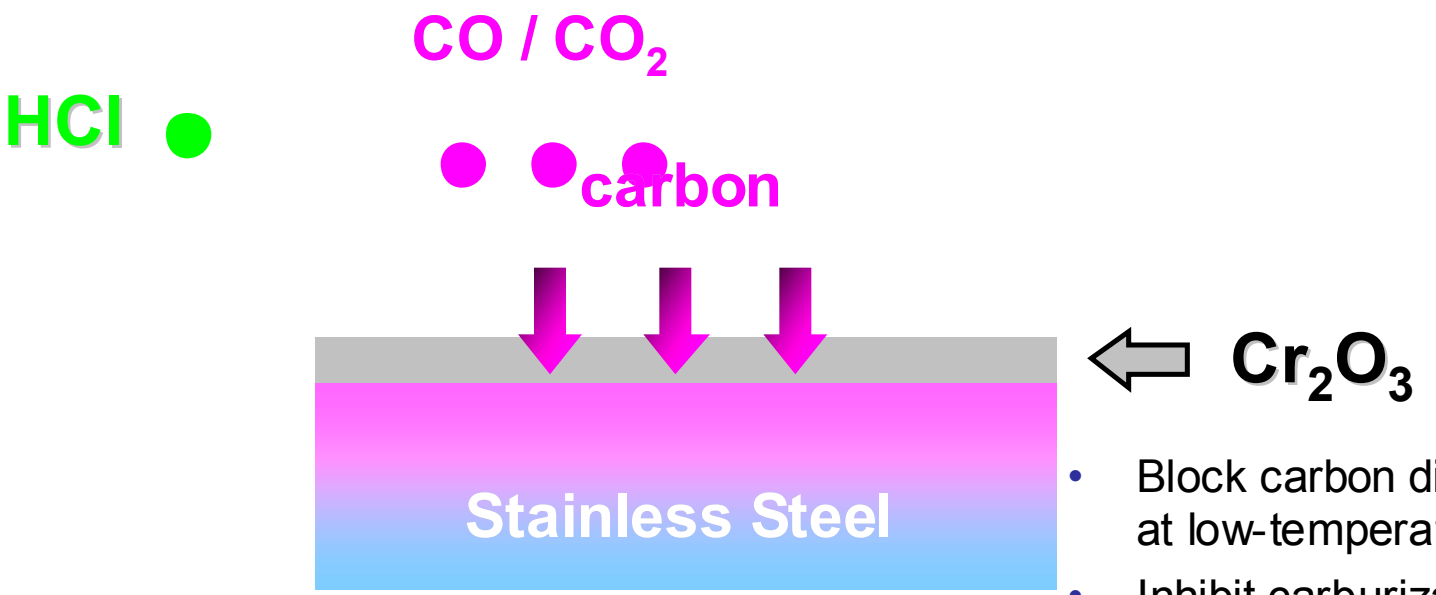
- Low-temperature colossal supersaturation (LTCSS) enhances the properties of 316 austenitic stainless steel
- Carbon concentrations of >10 at.% are readily achieved
- Hardnesses up to 1200 Vickers are achieved while maintaining ductility
- Enormous (2 GPa) residual compressive stresses are produced
- No carbide precipitation in treated 316: verified by TEM
- Corrosion resistance is greatly improved (600 mV increase in Ep)
- Treatment can be performed on finished components without distortion or change of dimension

Time-Temperature-Transformation Diagram for 316 Stainless Steel



Conventional carburization: 900 ~ 1000 °C (1173 ~ 1273 K)

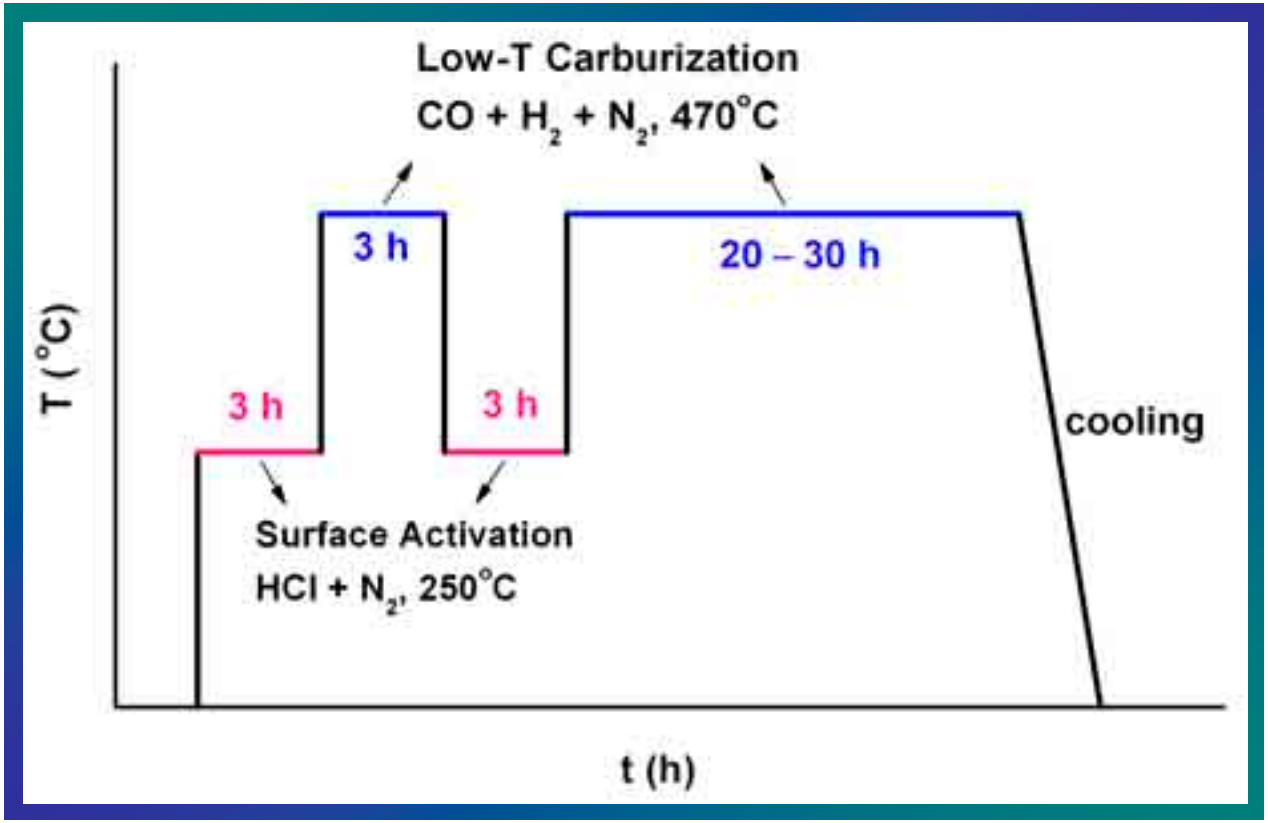
Surface Activation Treatment



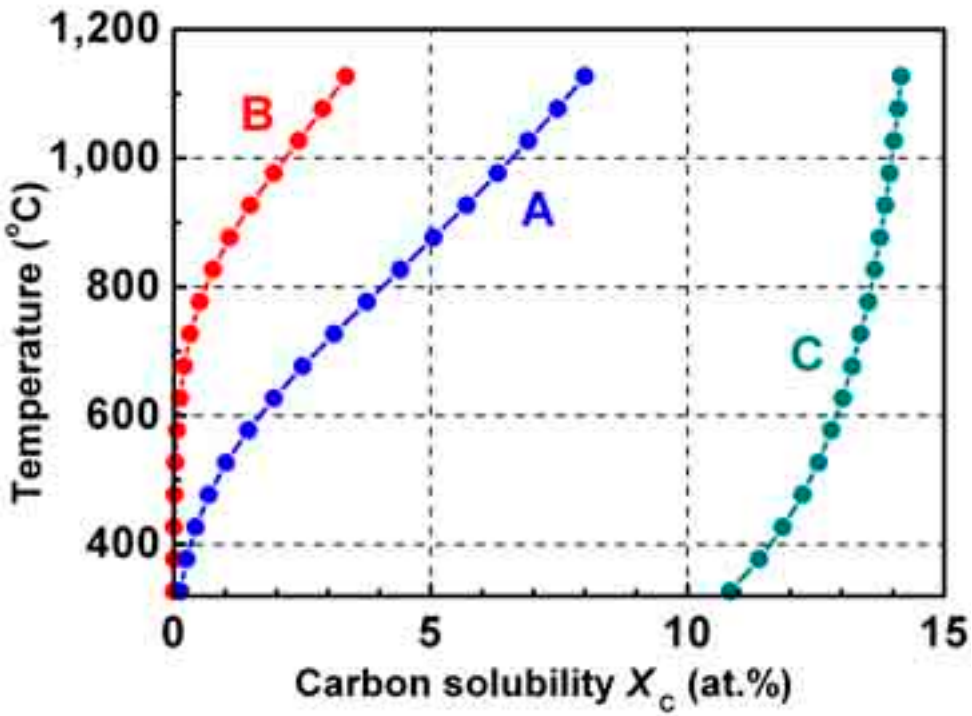
- Block carbon diffusion at low-temperature
- Inhibit carburization

- **Surface activation of the stainless steels prior to carburization is a key step that allows low temperature carburization to take place**

Low-Temperature Carburization



How Is LTCSS Possible?



A. Pure Fe

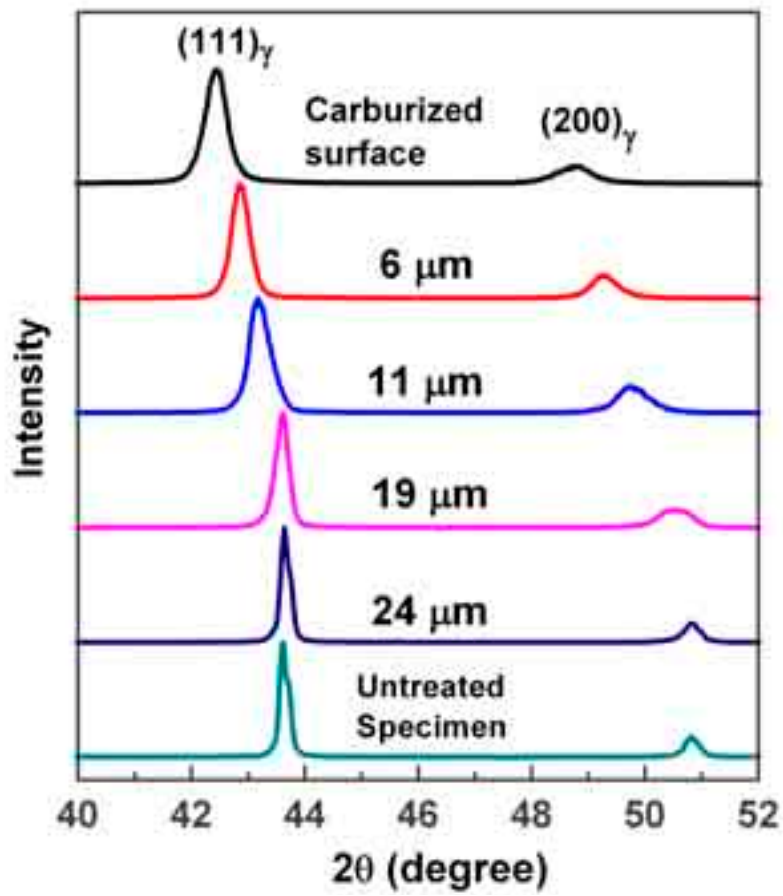
B. 316 SS, with Cr_7C_3 formation

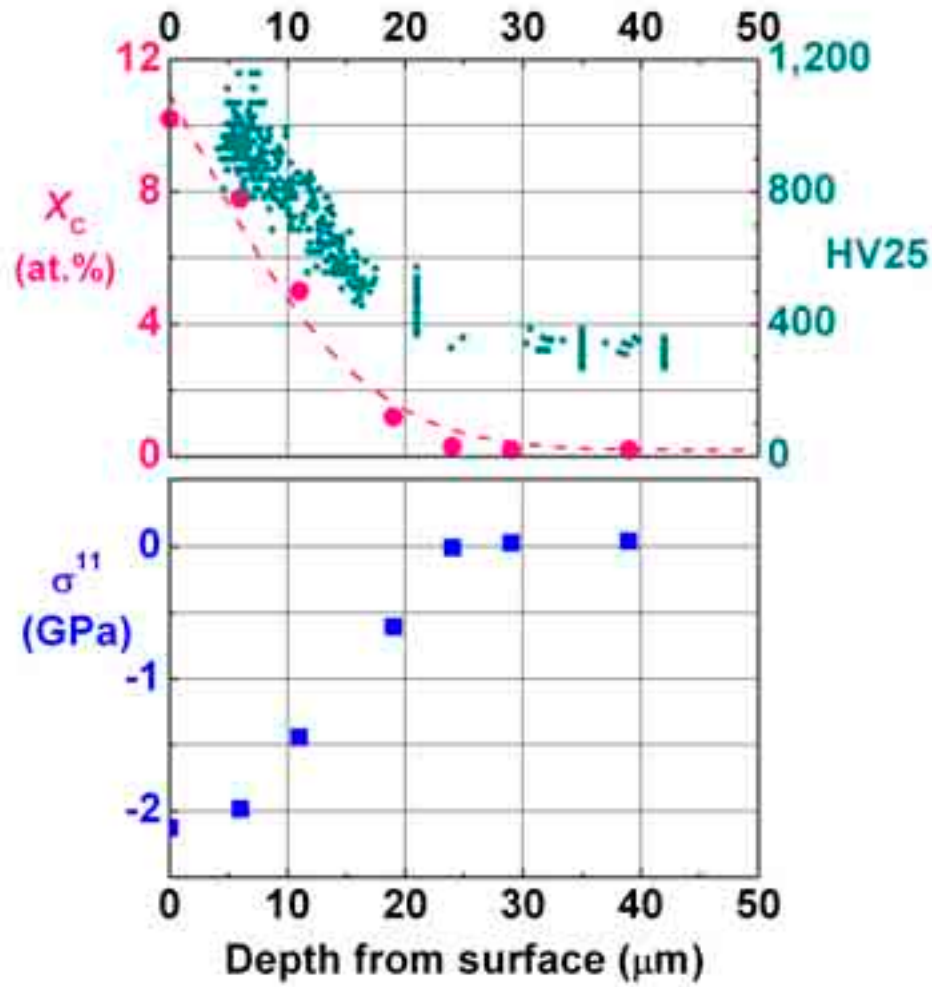
C. 316 SS, without Cr_7C_3 formation

Line A, for pure Fe, assumes the absence of ferrite. The presence of Cr (a strong carbide former) in 316 SS reduces the carbon activity coefficient in Fe, and hence the maximum solubility of carbon (line B). Absent carbide formation, the maximum *paraequilibrium* solubility of carbon is greatly enhanced (line C).

LTCSS Treated 316: XRD Depth Profiles

$a_\gamma = a_0 + \alpha X_C$
α = 0.00104 nm / at.%





Tasks 1, 2 and 3: Alloy/Specimen Acquisition, Treatment, and Initial Evaluation

Alloys Treated Successfully to Date:

- AISI 316, 316L, 316LN
- 254 SMO
- Inconel 625
- Incoloy 825
- 22-13-5 (XM-19 or Nitronic 50)
- AISI 304, 304L
- AISI 309
- AISI 310
- AISI 317
- AISI 321
- AISI 347
- AISI 303
- CF8M
- A286
- AL6XN
- 2209
- 13-8 Mo
- Hastelloy C22
- Biodur CCM
- MP35N

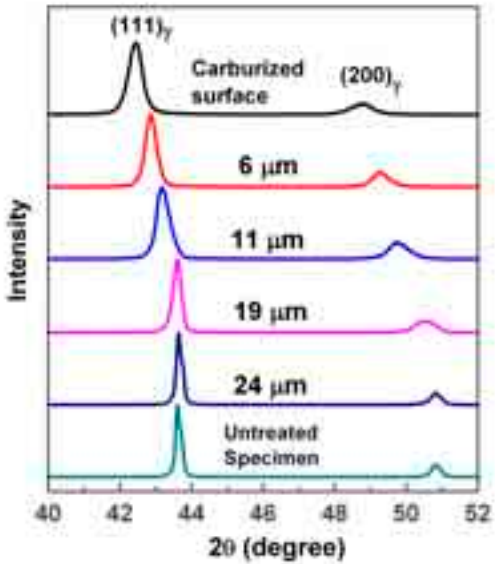
Tasks 1, 2 and 3: Alloy/Specimen Acquisition, Treatment, and Initial Evaluation

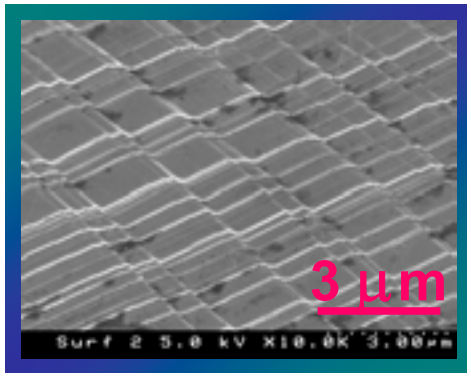
Additional Alloys Acquired for Assessment:

- AISI 201
- AISI 203 EZ
- Nitronic 60
- Biodur 108
- AISI 301
- CF3M
- AISI 316Ti
- Alloy 904L
- N 155
- L605

Task 4: Microstructural Characterization

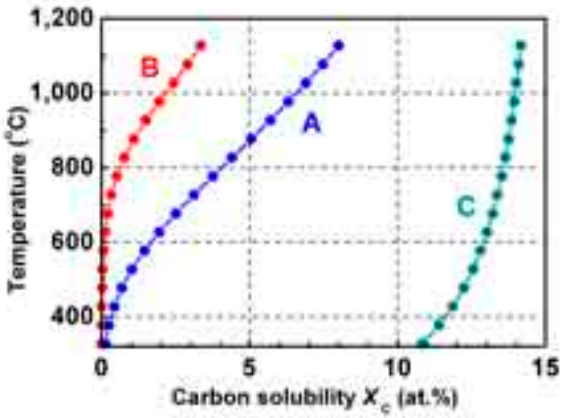
- XRD evaluation of treated materials verifies expanded austenite, no evidence of carbide precipitation
- Carbon concentration profile using Auger and EDS: 14 at.% in 254 SMO
- SEM of failed tensile specimen verifies ductility of treated layer
- Other techniques employed: TEM, OIM, SAM, CBED
- **FY06 Activities:** Develop correction method for Nelson-Riley plots for determining lattice parameter expansion of treated materials; continue characterization of treated alloys





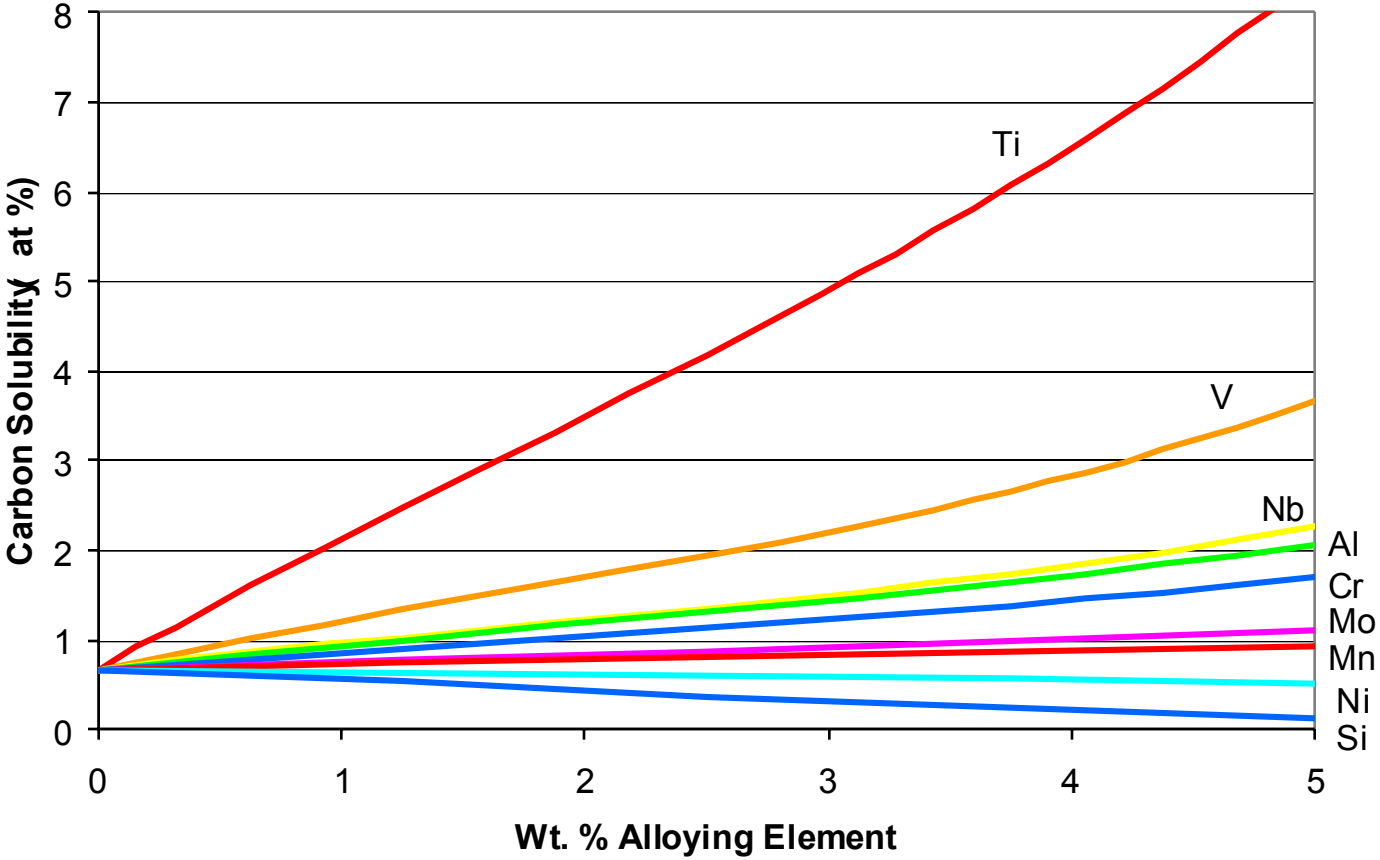
Task 5: Thermodynamic Modeling

- Solubility of carbon in austenite calculated as a function of alloying content
  - CALPHAD (Thermo Calc™) and Wagner dilute solution thermodynamic models developed
  - Elements considered: Fe, Cu, Ni, Co, Cr, Mn, Si, Mo, W, Al, V, Nb, Ti, Zr, N
  - Commercial alloys in test matrix modeled

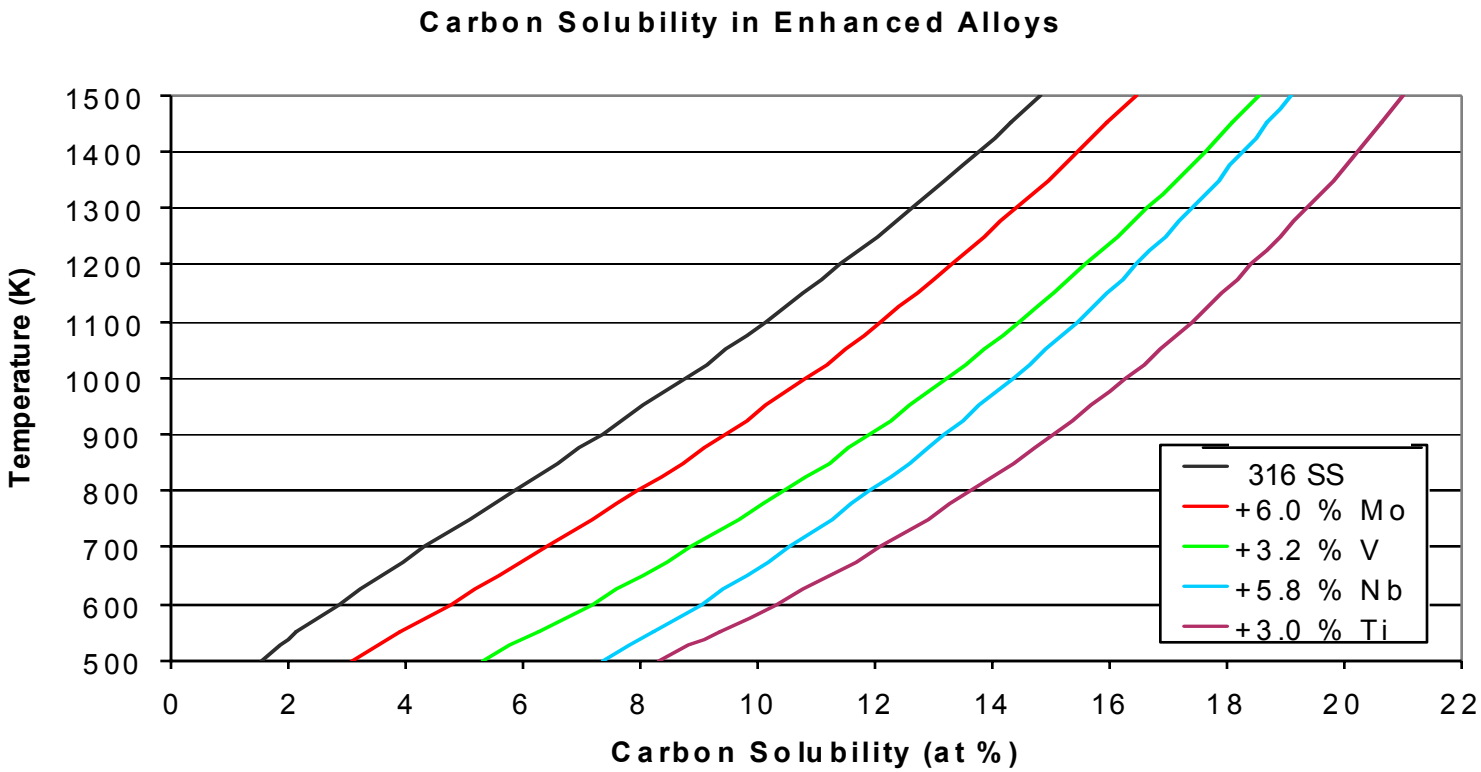


- Special efforts to obtain the necessary carbon-matrix element interaction parameters relevant to LTCSS
- Thermodynamic model used to design experimental alloys with enhanced affinity for carbon solubility at treatment temperatures
- **FY06 Activities:** Use experimental data from commercial alloys and experimental alloys to validate and refine model

Carbon Solubility in Austenite at 477°C as a Function of Alloy Content

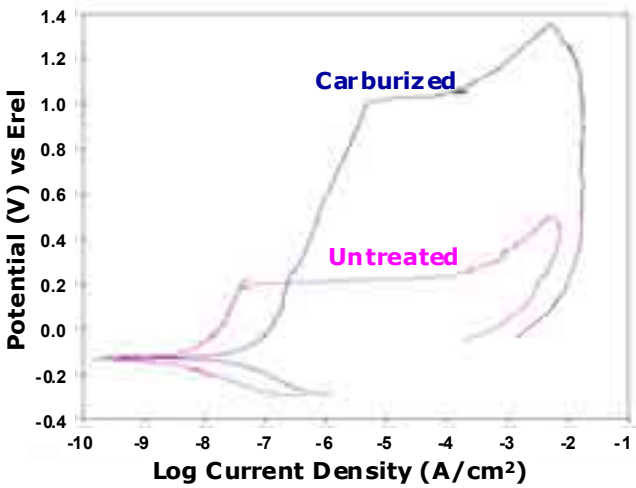


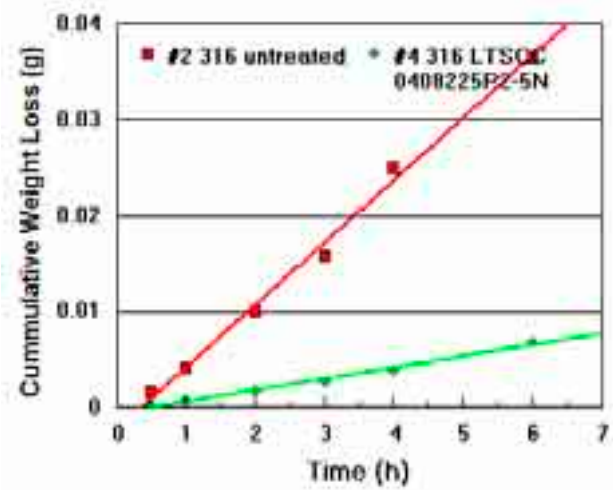
Alloy	C	Mn	Si	Cu	P	S	Cr	Ni	Other
1	0.01	0.50	0.20	0.50	0.01	0.001	20	18	3.0 Ti
2	0.01	0.50	0.20	0.50	0.01	0.001	20	18	3.2 V
3	0.01	0.50	0.20	0.50	0.01	0.001	20	18	5.8 Nb
4	0.01	0.50	0.20	0.50	0.01	0.001	20	18	6.0 Mo



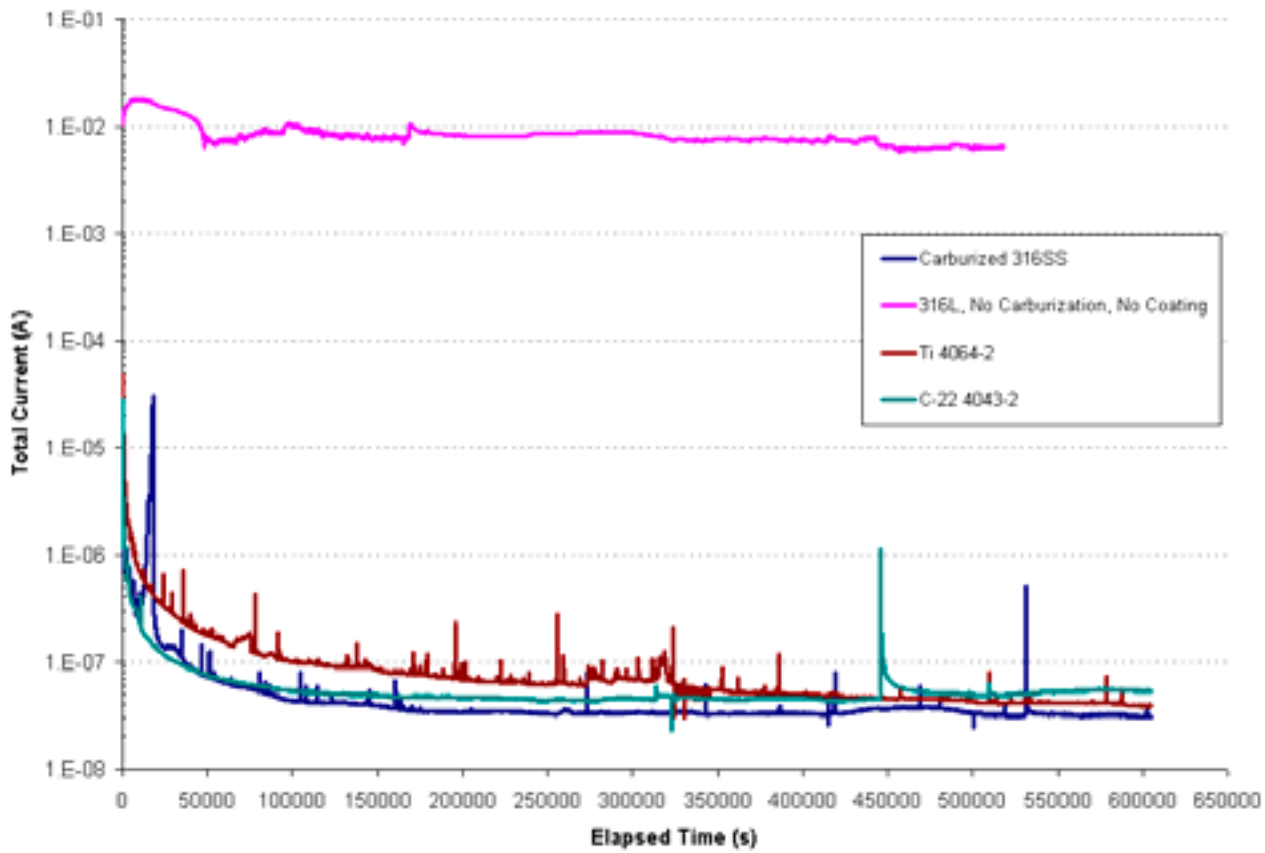
Task 6: Corrosion Testing

- Electrochemical polarization curves show 800 mV increase in pitting potential
- Treated tensile pull specimens (no residual compressive stress) show same behavior
- Erosion resistance: Cavitation tests up to 6 h show that treatment on 316 specimens reduces weight loss by a factor of approx. 5.5 times
- **FY06 Activities:** Stress corrosion cracking, crevice corrosion, continued erosion tests on other treated materials





Crevice Corrosion of Carburized 316L Stainless Steel vs. Wrought C-22 Alloy and Titanium 6-4



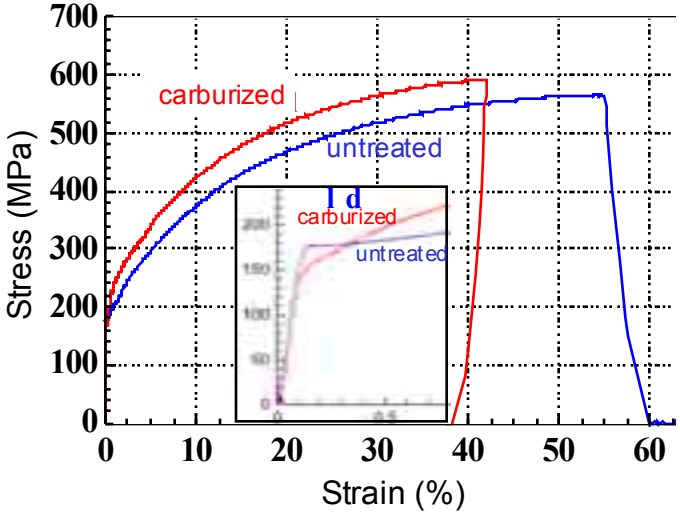
Untested Side

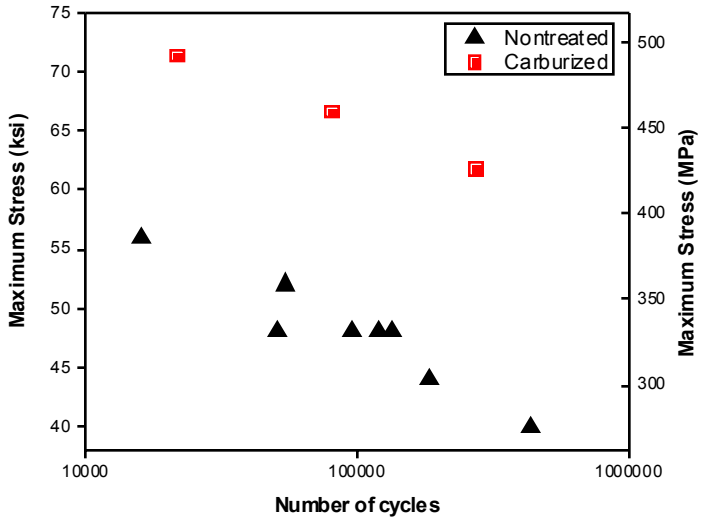
Tested Side – Post Test

Data courtesy of Naval Research Lab; 5 orders of magnitude improvement in crevice corrosion resistance for treated vs. untreated 316L

Task 7: Mechanical Testing

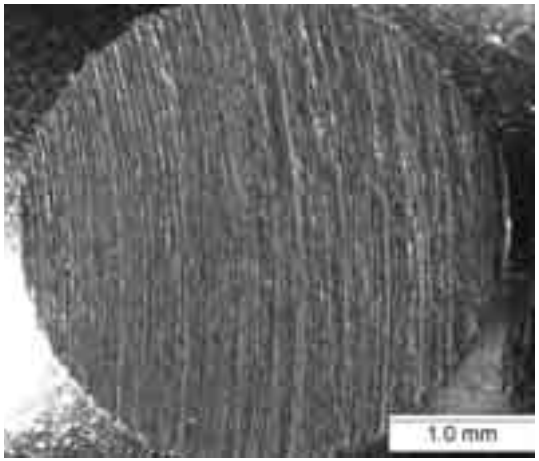
- Tensile testing complete on several treated alloys; ductility is maintained, UTS slightly enhanced
- Fatigue cycle life (R = -1) shows an order of magnitude improvement for the same max. stress level; max.design stress for infinite life improved by approx. 50%
- **FY06 Activities:** Continued testing activities on other treated alloys

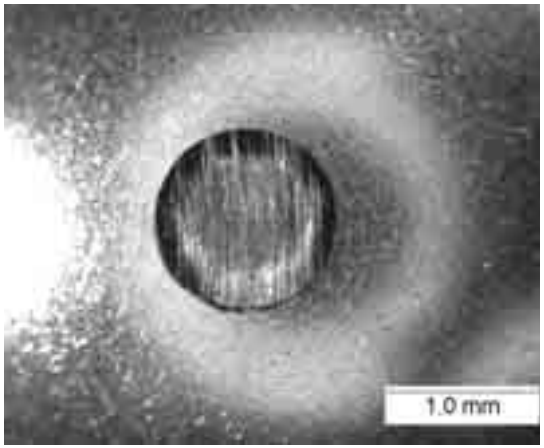




Task 8: Tribological Evaluations

- Pin on disk sliding friction and reciprocating friction tests: wear rates of treated couples (ball and disk) lowered by approx. 100 times compared to non-treated
- Continuous loop abrasion test (rotating abrasive belt): 30% reduction in wear volume treated vs. non-treated 316
- **FY06 activities:** Continued testing, evaluation of wear debris, sliding wear tests in salt water environments for wear/corrosion interactions





Task 9: Component Testing

- Components successfully treated for Jeffrey Chain (conveyor belt wear pins) and for Spirax Sarco (valve seats, pivot pins)
- Additional discussions underway with other industrial contacts
- **FY06 activities:** Industrial partners to evaluate treated vs. non-treated components in service for improvement in performance and energy efficiencies

Task 10: Manufacture of Experimental Alloys

- Using input from Task 5: Thermodynamic Modeling, 4 test heats have been melted, rolled and manufactured into test specimens
- **FY06 Activities:** Carburization treatments, microstructural characterization, and experimental verification of thermodynamic model

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1	0.01	0.50	0.20	0.50	0.01	0.001	20	18	3.0 Ti
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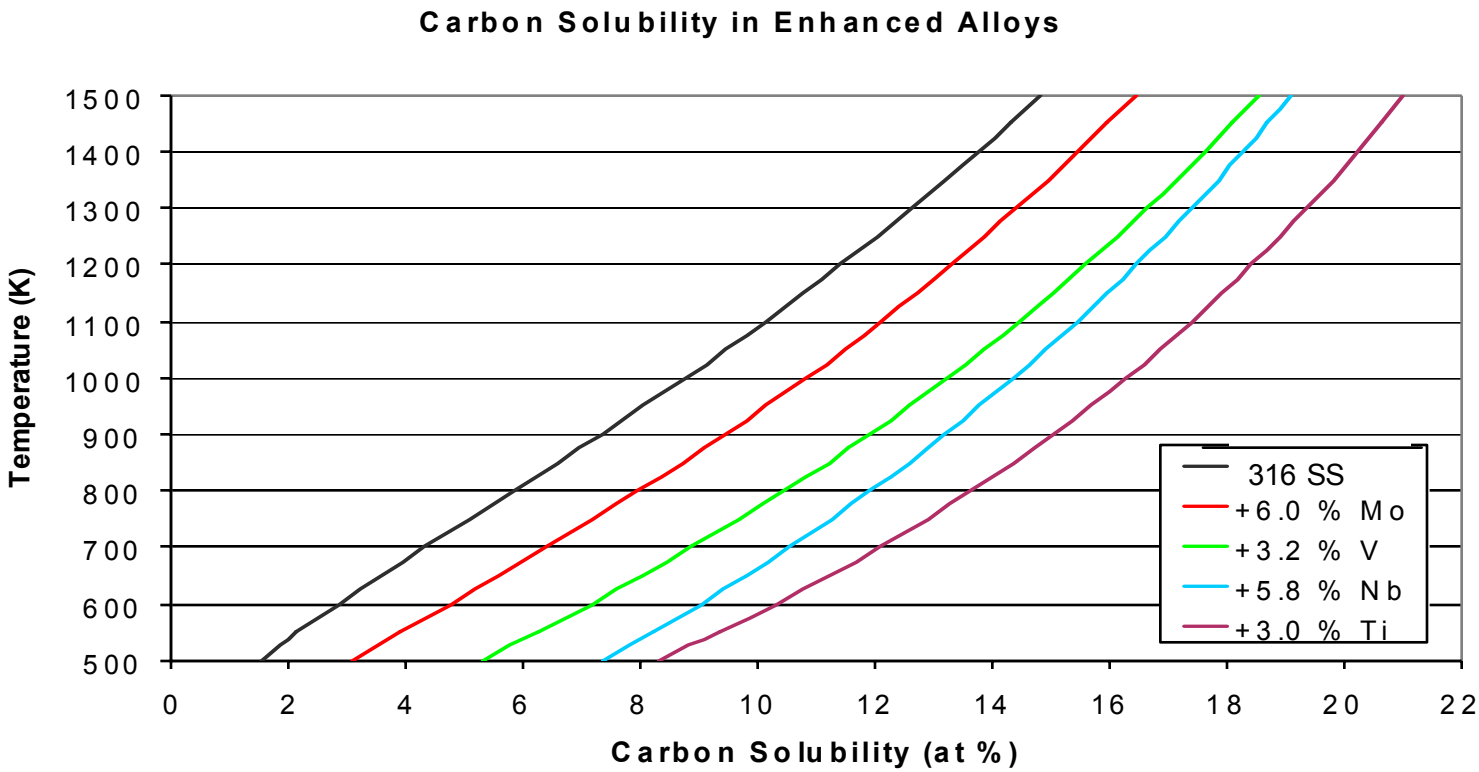

Presentations and Publications

- G. M. Michal, F. Ernst and Y. Cao, "Surface Hardening of Austenitic Steels by Low Temperature Colossal Supersaturation," presented at the *Symposium on Engineered Steel Surfaces: Nanotechnology, Hardness and Wear Resistance, MS&T'04* in New Orleans, September 2004 and submitted for publication in the *MS&T'04 Volume II – Engineering Steel Surfaces: AIST/TMS Proceedings*.
- P. J. Blau, J. Qu, and B. C. Jolly, "Wear Reduction of Austenitic Stainless Steels using a Novel, Low-Temperature Carburization Process," accepted for presentation the World Tribology Congress III, Washington, DC, September 2005, and submitted for publication in the proceedings.
- G.M. Michal, F. Ernst, H. Kahn, Y. Cao, F. Oba, and A. H. Heuer, "Impressive Carbon Supersaturation due to Paraequilibrium Carburization of Austenitic Stainless Steel," under review for publication in *Acta Materialia*.
- Peter J. Blau, Jun Qu, and B. C. Jolly, "Surface Engineering of Stainless Steel to Improve Wear Resistance without Sacrificing Corrosion Resistance." accepted for presentation at the 19th International Conference on Surface Modification Technologies (SMT 19), St. Paul, MN, August 2005, and submitted for publication in the proceedings.
- G.M. Michal, F. Eenst, and A. H. Heuer, "Carbon Paraequilibrium in Austenitic Stainless Steel," under review for publication in *Metall. Trans. A*.

Project Website

- http://pulex.cwru.edu/~ernst/private/Carburization/Pages/index.html

- user “LTCSS”
- password “colossal”
- URL, user, and password are case sensitive

Commercialization Activities