SAND2013-6139C

Basic Research of Intrinsic, Tamper-Indication Markings and Patterns Defined by Pulsed Laser Irradiation

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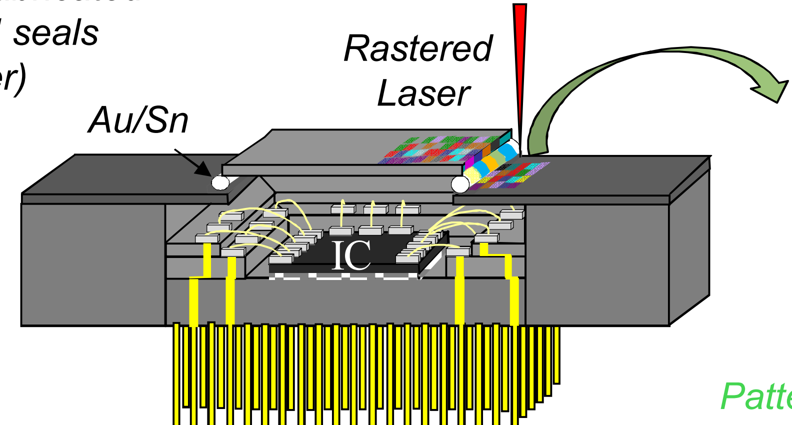
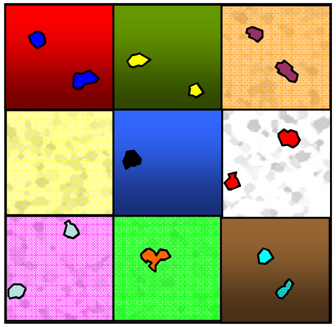
Novel Materials for Unattended Sensing to Support Future Treaties

<u>Primary Objective (from BAA):</u> "Identify microscale or nanoscale structures and phenomena in materials that can provide ***passive*** or active indicators of interference with unattended monitoring or sensing to support compliance with treaties."

OUR APPROACH: Research how short (ns) and ultra-short (fs, ps) pulsed laser light interacts with surfaces to create complex features and patterns for use as passive indicators of interference/tamper

Ex. Color patterns fabricated across metallurgical seals (welds, braze, solder)

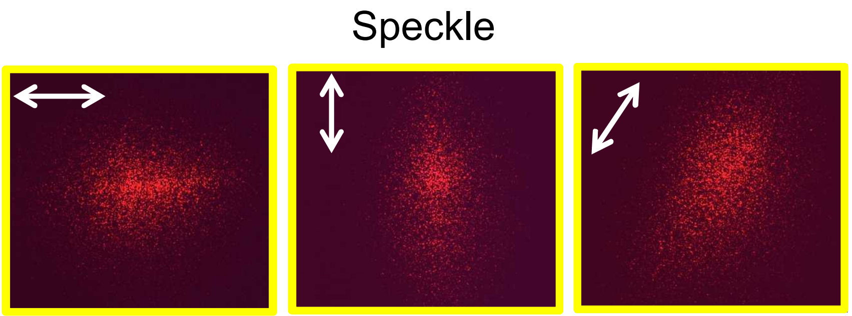




Archived after fabrication

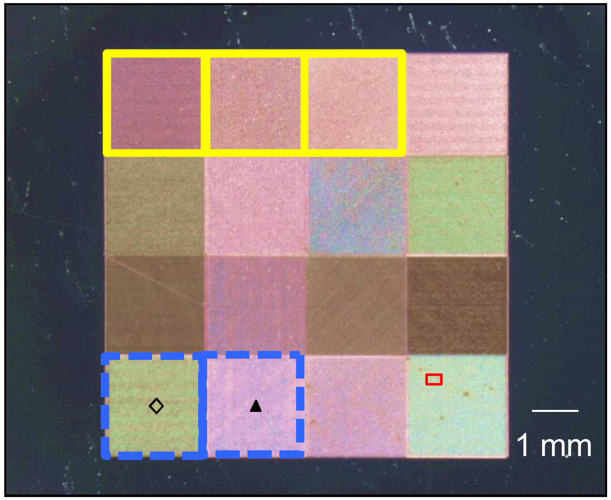
Pattern rapidly interrogated in field and compared to determine authenticity

Color markings consist of different archivable features.

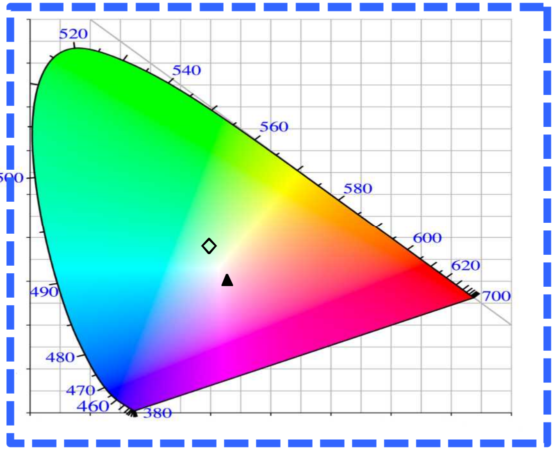


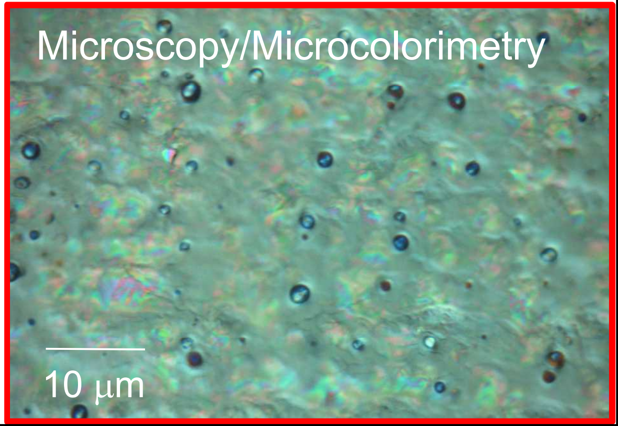
- Tailored characteristics include:
  - pre-designed color features, patterns
  - periodic scan lines of specific direction, hatch

- Intrinsic nano-scale color features are:
  - isolated precipitates in large area pattern,
  - often a unique color
  - randomly positioned / sized



Spectrophotometry
Chromaticity



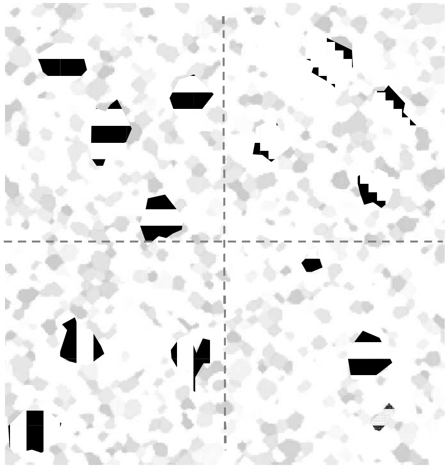


Macroscale color patterns can also be used as maps to guide interrogation of small color features

Periodic surface morphology is also under investigation for use as a unique identifier.

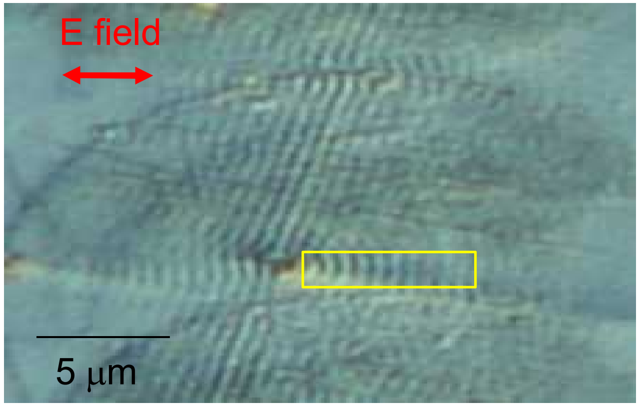
- Tailored characteristics of ripples include
  - wavevector (set by laser polarization)

- Random / intrinsic characteristics include
  - location and size of rippled areas (via asperities)
  - ripple periodicity (via surface plasmons)
  - ripple amplitude (varies with distance from source)

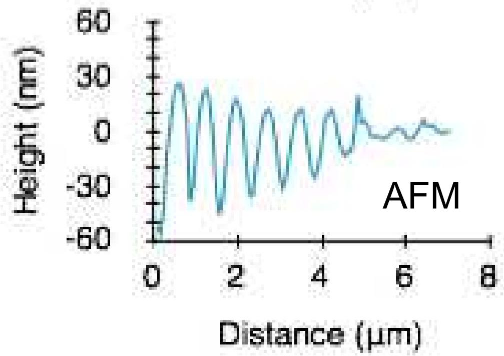


Periodic ripple pattern on stainless steel 304L

1.2 J/cm^2, 150fs, 780 nm in air



Shifted periodicity (from 780 to 740 nm) attributed to plasmon polaritons



Rapid, non-destructive methods for interrogation include diffraction, microscopy.

Rapid laser marking processes are desired for fabricating a variety of different features.

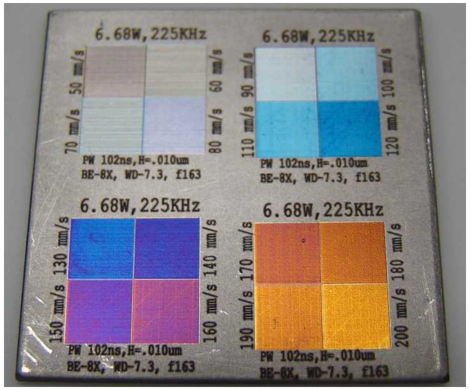
Our approach: rastered, pulsed laser spot (ns or fs)

- Color markings: Metal reacts with air to form coating
- Ripple markings: Pulsed laser roughens surface

Stainless Steel 304L

- Variety of materials form color layers when using a 1064 nm, ns-pulsed fiber laser
  - Stainless steel 304L: R (ϕ = 0°) = 0.73
  - Dual phase steel (50% ferrite): R (ϕ = 0°) = 0.72
  - Titanium CP2 grade: R (ϕ = 0°) = 0.57
  - Titanium alloy Ti6Al4V: R (ϕ = 0°) = 0.37
  - Kovar™ (FeNiCo): R (ϕ = 0°) = 0.63
  - Georo™ (Au88Ge12): R (ϕ = 0°) = 0.74

Titanium (CP2 grade)



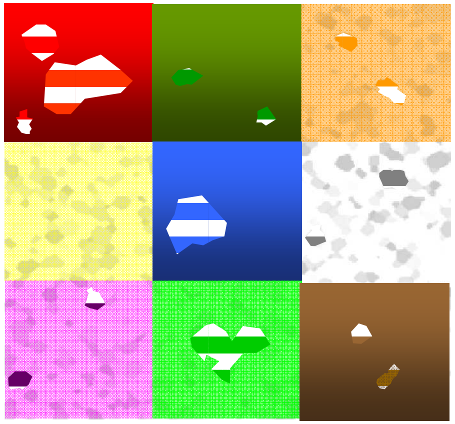
1 cm

- Large variety of materials develop ripple patterns when irradiated by a 800 nm, fs-pulsed laser
  - Silicon, Stainless Steel, Ti.

Technical Objectives of Current Year

<u>Research of</u>

- Mechanical properties of laser-defined color oxide layers
  - Toughness
  - Coefficient of friction
- Heat affected zones resulting from scanned, ns laser irradiation
  - Thermal modeling of pulsed heat input
  - Multiple substrates
- Complex markings that combine periodic ripples, colors
  - All-in-one process involving ns irradiation
  - Two step process involving ns and fs irradiation
- Stability of laser-fabricated markings
  - Normal aging (room temperature, multiple years)
  - Accelerated thermal aging (elevated temperature, short time)



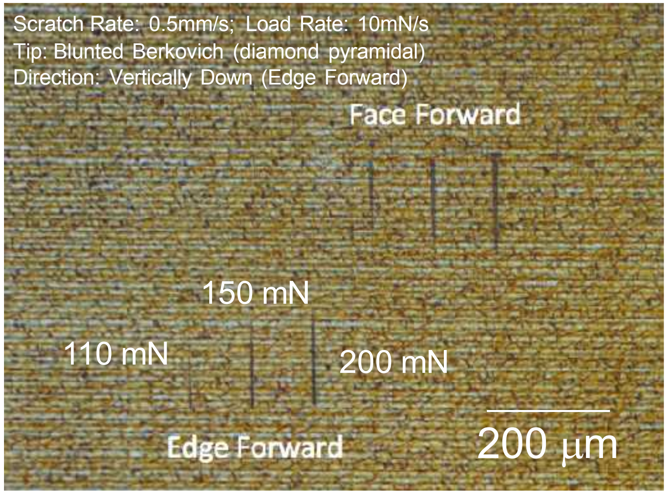
Hypothesis

An additional Year 3 task involved publishing results from Year 2.

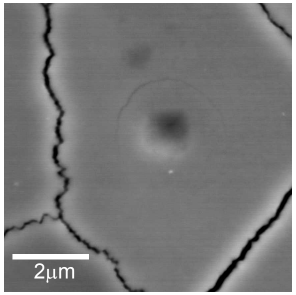
In FY13, the mechanical properties of laser-grown oxides were evaluated to gauge long term use.

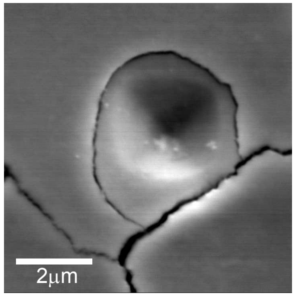
- Micrographs from nanoscratch testing show no evidence for spalling or interfacial fracture.
- Micrographs from nanoindentation show circumferential cracking at the plastic zone radius but no evidence of spalling.
- Oxides tested included those made on Ti and stainless steel.

Nanoscratch Tests



NanoindentationTests





No evidence for interfacial fracture is consistent with a large interfacial toughness.

Colored oxides made on stainless steel and Ti exhibit large interfacial toughness and coefficient of friction.

- fracture toughness, K

Substrate	K_{ox} (MPa √m
SS 304L	2.05-3.2
Ti (CP2)	1.77-2.67

- coefficient of friction, C_f

Substrate	C_f
SS 304L	0.15-2.0
Ti (CP2)	0.05-0.09

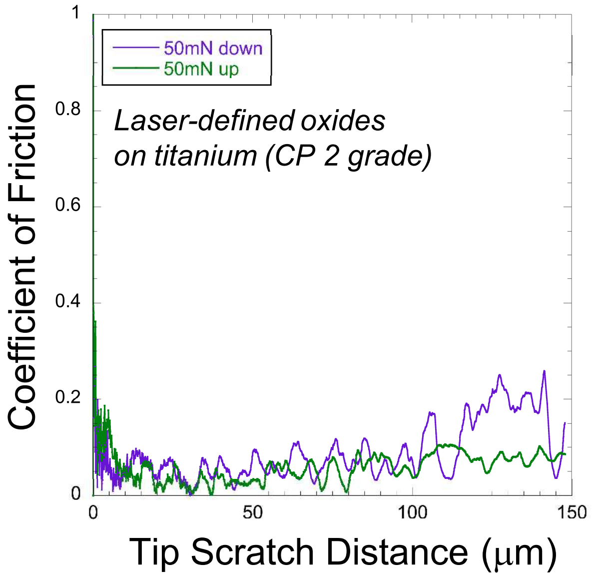
- Modulus hardness

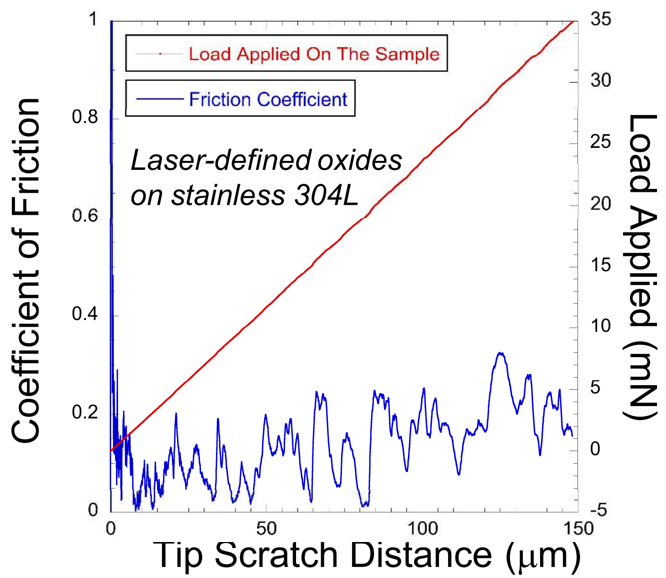
Substrate	E_{ox} (GPa)	H_{ox} (GPa)
SS 304L	137-208	9.5-12.3
Ti (CP2)	199-251	15.1-16.4

What does this mean?

1.) All oxide layers on steel and Ti are adhered well

2.) Oxide layers have good wear resistance (between that of a hard metal and alumina (gauged from H/E ratio) ref. W. Yi-Ling et al., Wear 1988)*





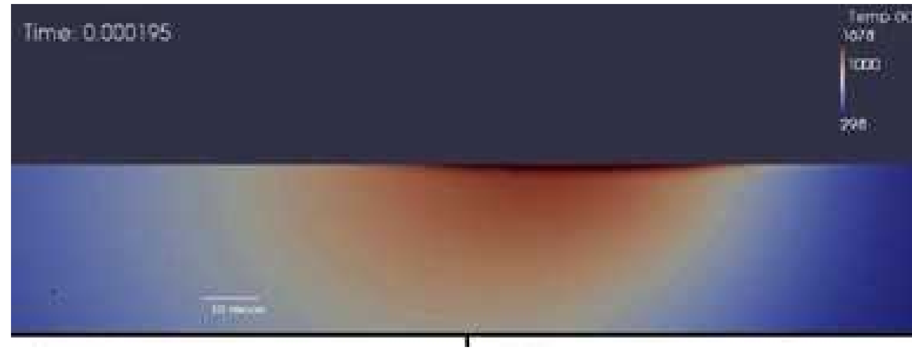
Thermal modeling has been used to predict Heat Affected Zones (HAZs) for scanned pulsed laser irradiation.

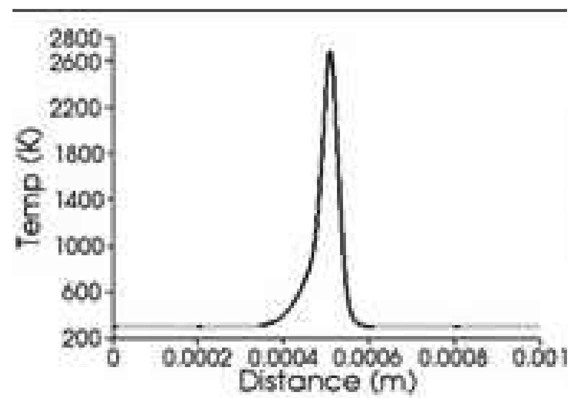
- Thermal model treats a scanned, pulsed, Gaussian-shaped laser beam incident on a polished surface.

- Models account for
  - substrate reflectivity (or film %R)
  - temperature dependent phys. props. (κ, C_p)
  - radiation loss boundary conditions, $\varepsilon = 0.4$
  - beam characteristics (P_{avg}, λ, etc.)

- Simulations used the Sandia Red Sky supercomputer and implemented Sierra Mechanics FEM code (grid size 0.1 μm)

- Target materials modeled include SS304L,Ti, two phase steel,Ti w/ thin ox



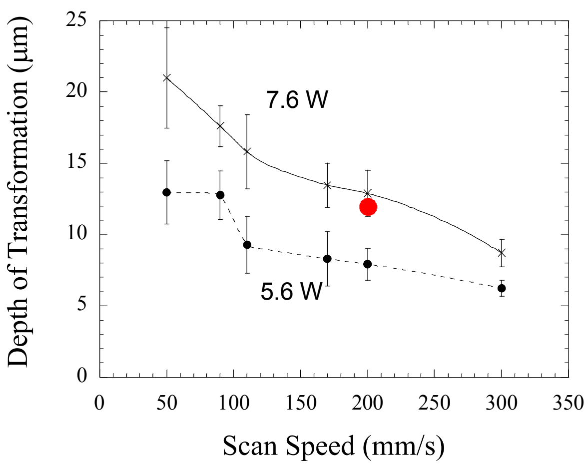


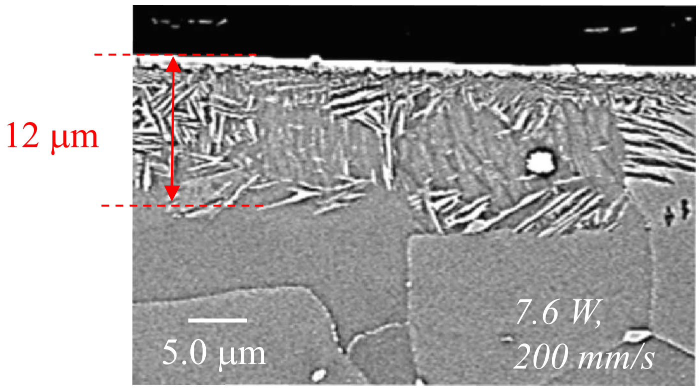
Models of our laser color marking processes demonstrate there is minimal temperature increase at 500 μm depth.

Model predictions of HAZs were validated by electron microscopy.

Results with Ti

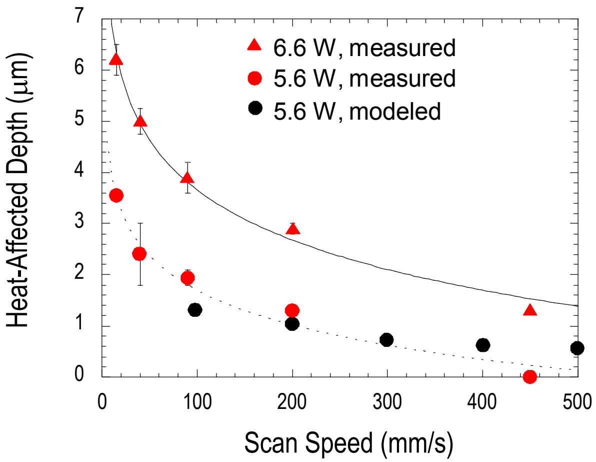
- Models predict depths to T = 915°C (β transus)
- Probed by SEM, inspecting for α' martensite

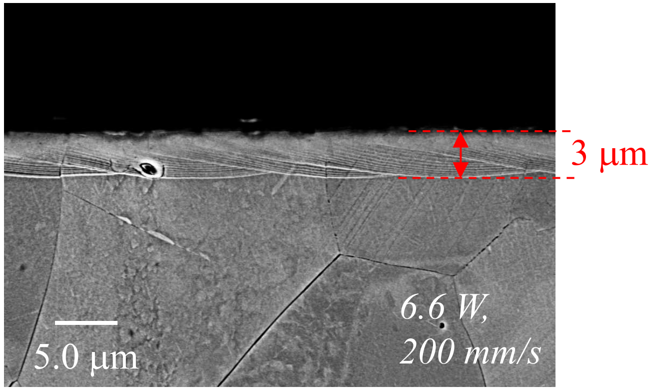




Results with Stainless Steel

- Models predict melt depths (T_{melt} = 1427°C)
- Probed by SEM, observation of melt

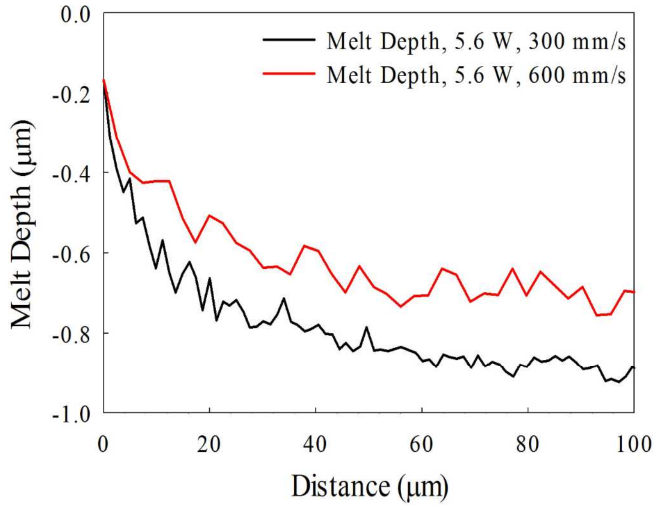




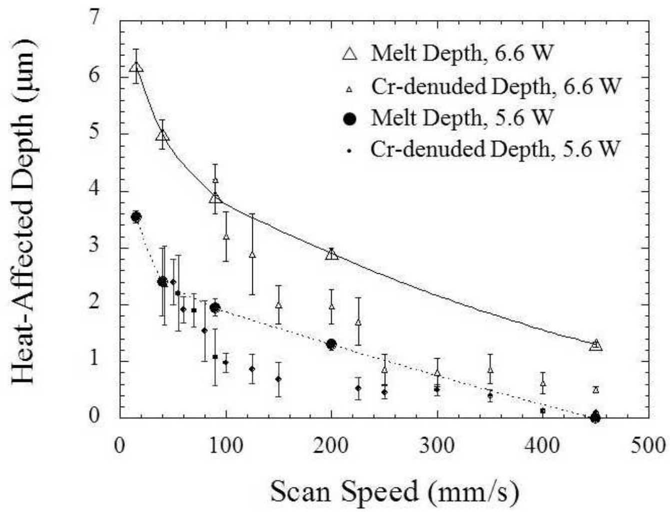
Models of scanned laser irradiation show other key elements of design.

- Thermal models predict that melting reaches steady-state (uniform depth) after beam travels approx. 60-100 μm from edge of feature.

- Infer minimum feature size is ~ 500 μm (this assumes formation of a uniform colored center that is 5x width of boundary color)



Model Predictions: Irradiation of SS304L

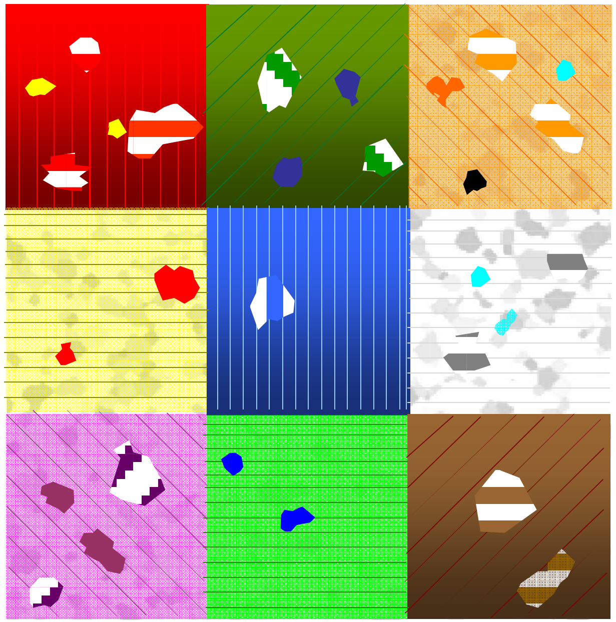


Experiments showing Cr-denuded depths ~ melt depths

Combination of color and periodic ripples should establish more complex markings that are virtually impossible to duplicate.

Example macroscale color pattern depicted on right wherein each square 'macro-pixel' has

•a tailored color
•a tailored scan line direction, hatch



Random features includes

•isolated color precipitates
•periodic ripple patterns formed at
random sites, covering irregular-sized areas

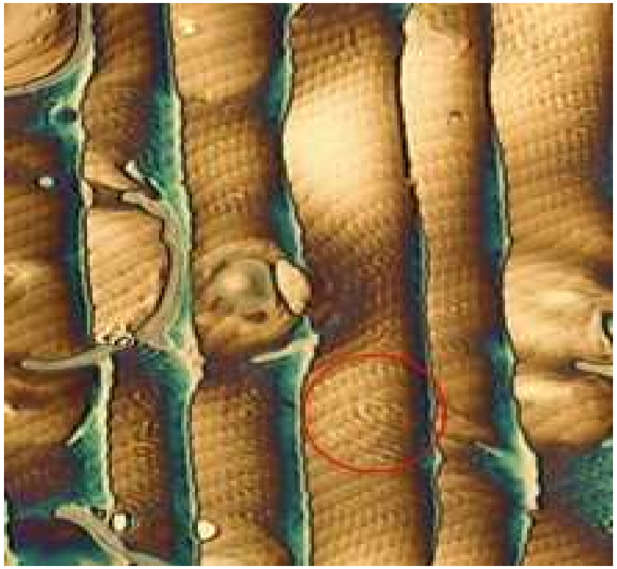
In Year 3, hybrid processes were studied including single step nanosecond pulsed irradiation and two step nano/femtosecond irradiation

Scanned, nanosecond-pulsed laser irradiation has been used to simultaneously generate color features and localized ripples.

Example macroscale color pattern depicted on right wherein each square 'macro-pixel' has

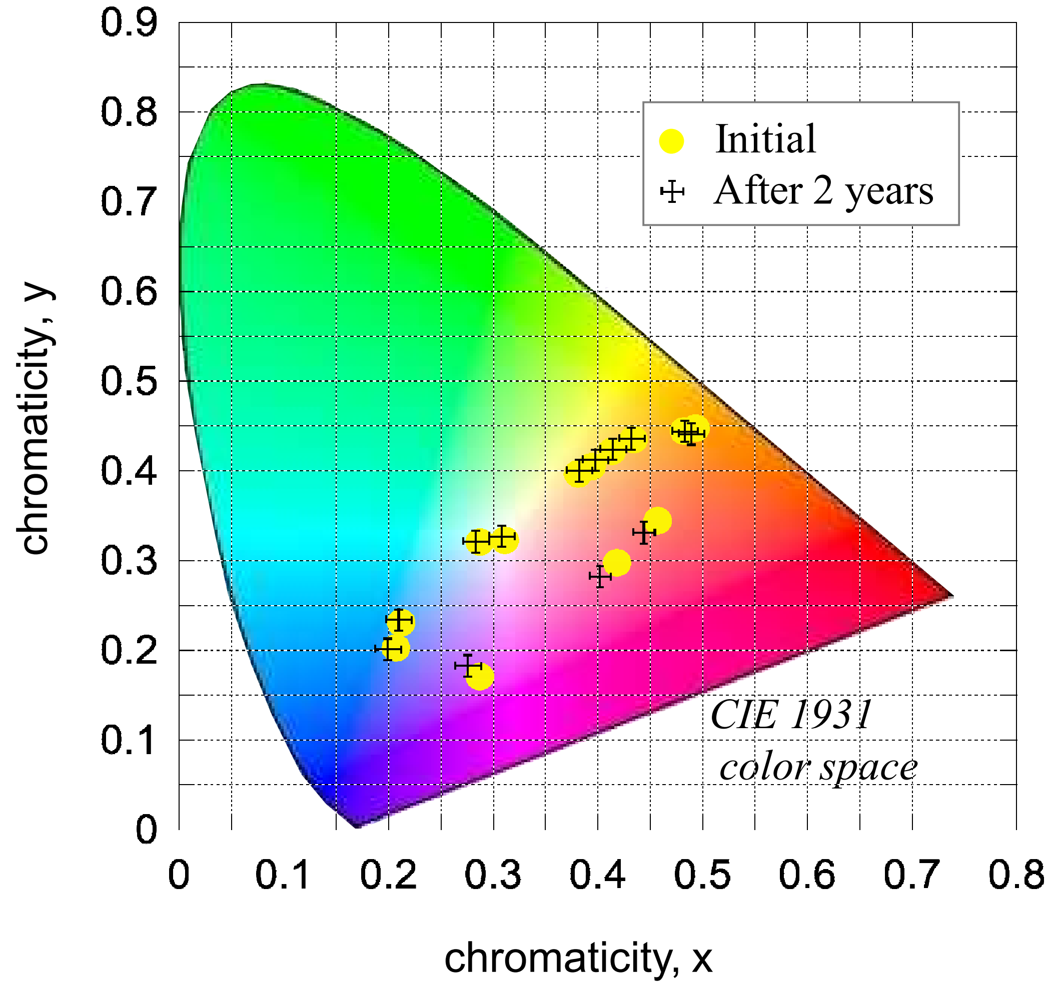
•a tailored color
•a tailored scan line direction, hatch

Are combined color features and ripples too complicated for rapid interrogation / analysis in the field?



Optical properties of color layers have not changed significantly over two years (normal aging).

- 200 samples tested by aging at 75°F, 40% relative humidity, lighted room
- Tested samples were various oxide coatings made on SS304L, Ti
- No detectable change in chromaticity (within uncertainty)
- No detectable change in spectral reflectance (within uncertainty)

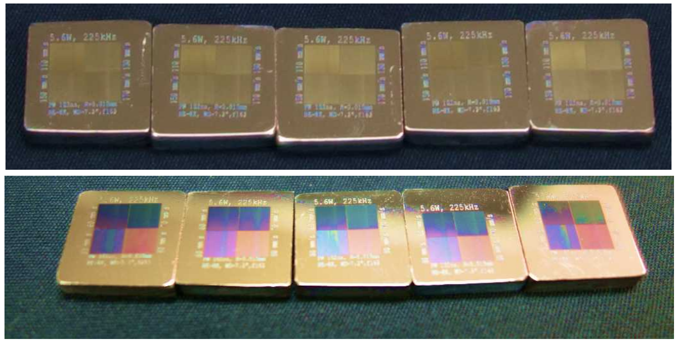


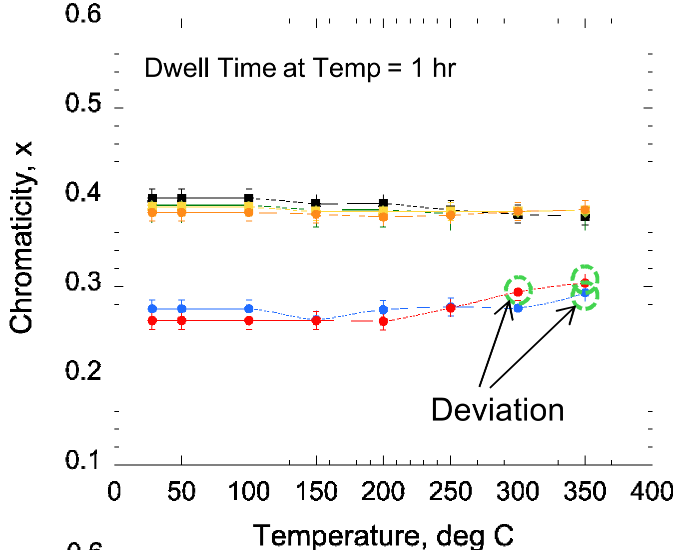
Also, there are no detectable changes in colored, micro-precipitates after 2 years.

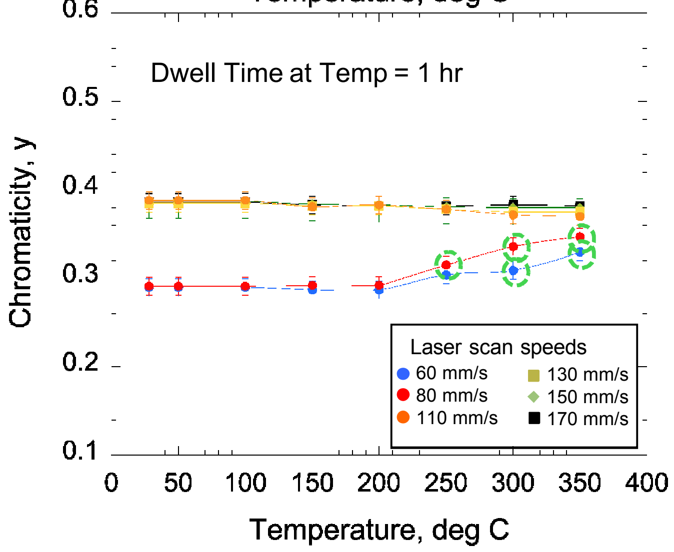
Accelerated aging at high temperature reveals high decomposition temperatures (~250°C) for colored oxides.

- No detectable change in chromaticity (x,y) below 200°C for multiple hours.
- No detectable change in spectral reflectance below 200°C for multiple hours.
- We turn to XRD for phase identification associated with transformation

Ex. Oxides made on Ti6Al4V were aged at high temperature







Eleven Presentations in past year (21 total for project)

Invited: D. Hirschfeld ASM-ASME Local Chapter Symp. (Albuquerque, 11/14/12).

Contributed: S. Lawrence Int. Conf. on Metal. Coatings and Thin Films (San Diego, 5/1/13).

Contributed: R.D. Murphy 2013 Conf. Lasers and ElectroOptics, CLEO (San Jose, 6/10/13).

Contributed: R.D. Murphy 2013 Conf. on Lasers and ElectroOptics, (San Jose, 6/10/13).

Contributed: R.D. Murphy. Materials Research Soc. Fall Meeting (Boston, 11/29/12).

Contributed: S. Lawrence et al. TMS Annual Meeting (San Antonio, 3/5/13).

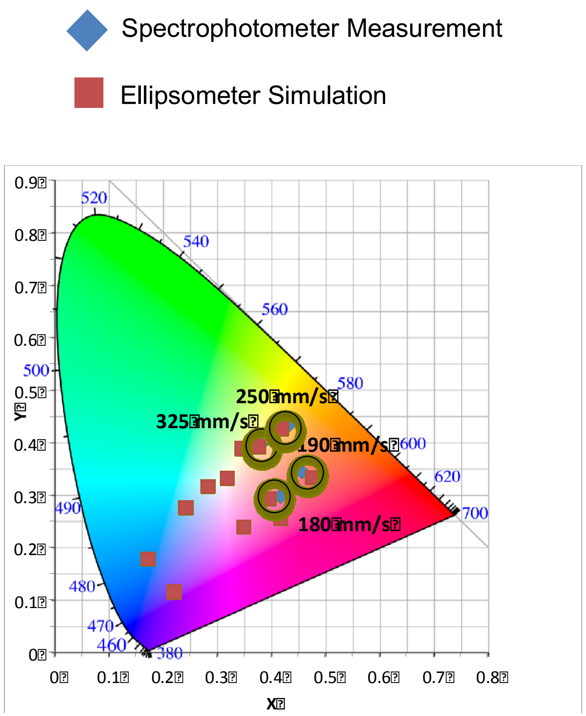
Contributed: S. Lawrence et al. Corrosion 2013 (Orlando, 6/10/13).

Contributed: S. Lawrence SSGF 2013 Annual Mtg (Santa Fe, 6/26/13).

Contributed: R.D. Murphy et al. AVS NM Chapter Symposium (Albuquerque, 5/22/13).

Contributed: S. Lawrence et al. Materials Research Soc. Fall Meeting (Boston, 111/27/12).

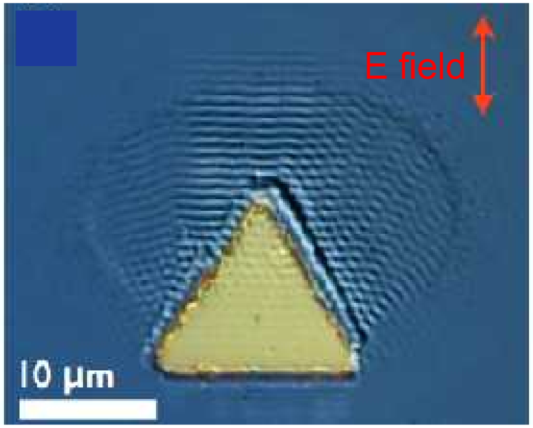
Contributed: D. Saiz. AVS NM Chapter Symposium (Albuquerque, 5/22/13).

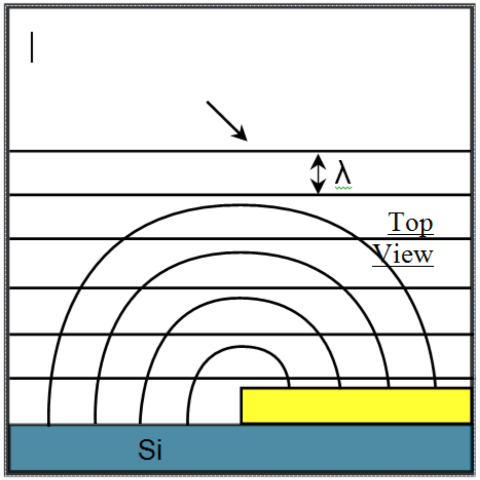


Predicting structure-property relationships and validating these predictions

Three publications and one award in past year (6 total for project) and one dissertation

Ripple formation on Si due to light scattered from a gold mesa and model explaining effect





Peer-reviewed Publications (3)

Applied Physics Letters, "Pump-Probe Imaging of Laser Induced Periodic Surface Structures after Ultrafast Irradiation of Si", Manuscript # *XXYY* - *Full DTRA support*

Surfaces & Coatings Technology, "Nanosecond Pulsed Laser Irradiation of Titanium: Oxide Growth and Effects on Underlying Metal", Manuscript # *XXYY* - *Full DTRA support*

Surfaces & Coatings Technology, "The Mechanical and Electromechanical Behaviors of Oxide Coatings Grown on Stainless Steel by Nanosecond Pulsed Laser Irradiation ", Manuscript #*S-13-02083* *Full DTRA support*

Award (1)

Best Student Poster Award: R.D. Murphy with "Formation of Laser Induced Periodic Structures", AVS-NM Chapter Symp., May 22, 2013 - *Full DTRA support*

Dissertation (1)

R.D. Murphy, Applied Physics PhD, Univ. of Michigan *Partial DTRA support*

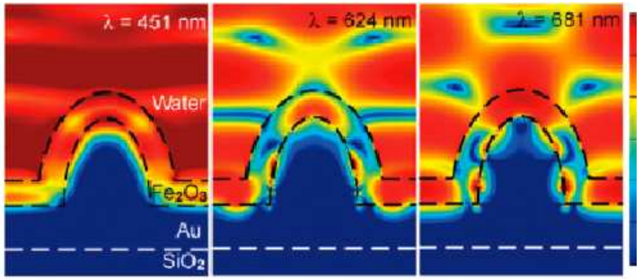
Summary

- Pulsed-laser color marking of oxidation of metals and alloys
  - Complex, macro-scale color patterns can be tailored
  - Large palette of readily-identifiable colors (R, x, y)
  - Site-specific, micro-scale color precipitates form within larger patterns
  - Detailed optical properties (n,k) measured; colors can now be predicted
  - Oxide coatings adhere well, are hard and exhibit good wear resistance
  - Oxide coatings are stable over time and for moderate temperatures
  - Detailed structure-property relationships identified for oxides on Ti, SS304L

- Nano-scale ripples are a second form of archivable markings.
  - Ripple patterns form with small distribution of wavelengths
  - Wavevectors tailored by incident polarization
  - Site-specific ripple formation at local protrusions during scanned laser processing
  - Origin of ripple patterns identified (interference of scattered light with impinging light)
  - Ripple periodicity affected by surface plasmon polaritons
  - Time scales for surface ripple formation (~ 50 ps) demonstrated by ultrafast pump-probe microscopy

Proposed Year 4 tasks would build on prior year's research.

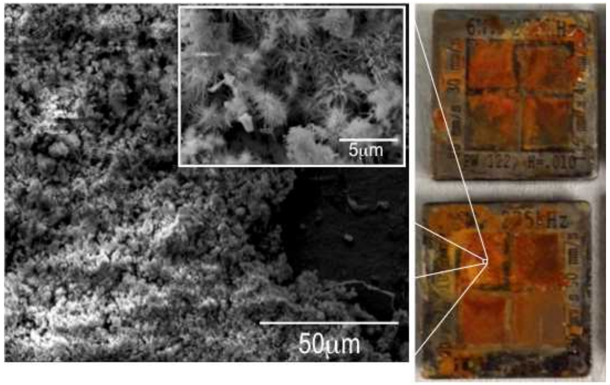
- **Modeling formation of laser-induced periodic structures**
  Sub-task 2.4 Investigate role of surface plasmon polaritons, effects of fluence, site specificity
  Sub-task 2.5 Model light solid interactions using EM solver (Lumerical) multi-source scattering, interference



Predicting enhanced optical absorption near asperities

- **The stability of laser-defined markings**
  Sub-task 6.4 Corrosion testing, implements salt fog and salt spray tests

- **Methods for rapid feature interrogation**
  Sub-task 7.1 Investigate light-based methods including diffraction, methods that implement long sampling distances including speckle



Our initial test: markings on SS304L, salt water (after 1 mo.)

BACKUP SLIDES

University Collaborations in 2013

- Sub-contract extended with Univ. of Michigan
- Ryan Murphy (Applied Physics grad. student)
  Graduated with PhD : 2/2013 (100% commitment)
  Now a post doc at Sandia working with this team
- Basic research of surface roughness evolution during pulsed laser irradiation involving ultrafast pump-probe microscopy


- Sub-contract extended with Purdue Univ.
- Samantha Lawrence (Materials Science & Engineering
  Expected PhD date: 2014, 25% time commitment
- Research of the mechanical properties of laser-fabricated metal oxides (includes study of hardness, adhesion, phase, variations through thickness)


All students and professors are US citizens

Technical Objectives for FY11 have been completed

- Research pixel-by-pixel control of laser color features using 10-200 ns light
- Research effects of pulse frequency on color layer formation
- Investigate microstructure, composition, optical properties of color layers
- Research hardness and modulus of color layers (nanoindentation)
- Implement a thermal modeling code to simulate the effects of laser irradiation (fixed position, varies pulse duration, rate, energy per pulse, wavelength)
- Qualify ultrafast pump-probe instrument (Univ. of Michigan)
- Research temporal evolution of laser-induced periodic surface structures

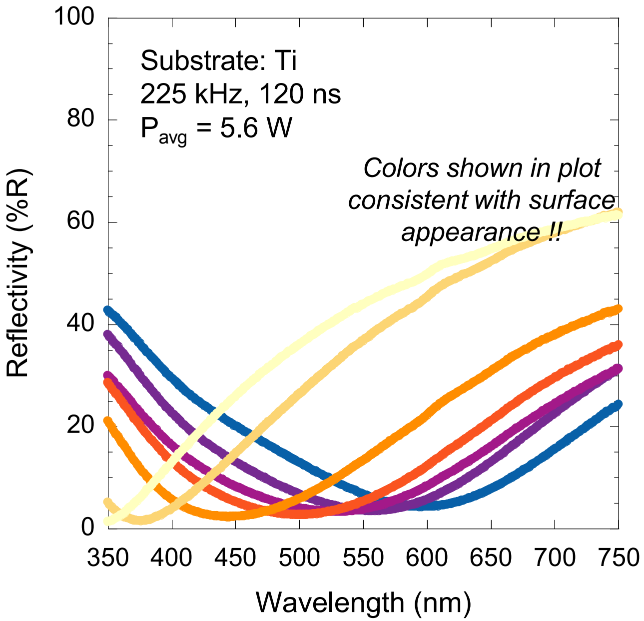
Sandia National Laboratories

Color information can be archived in several forms.

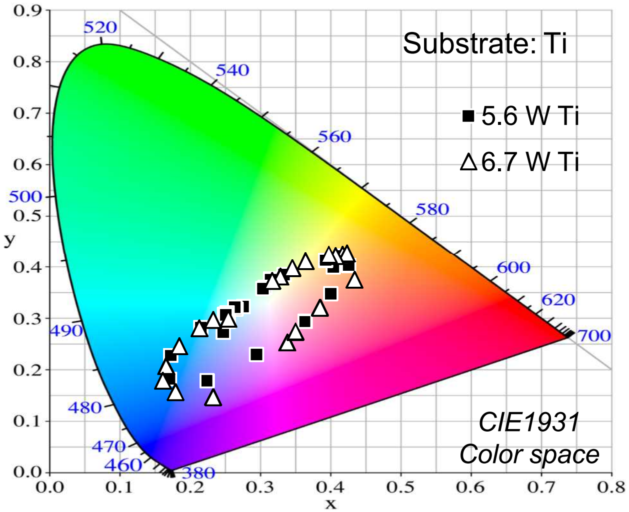
Visual photograph / micrograph

1 cm

Reflectance Spectra (obtained from individual pixels)



Chromaticity (x,y) (obtained from individual pixels)

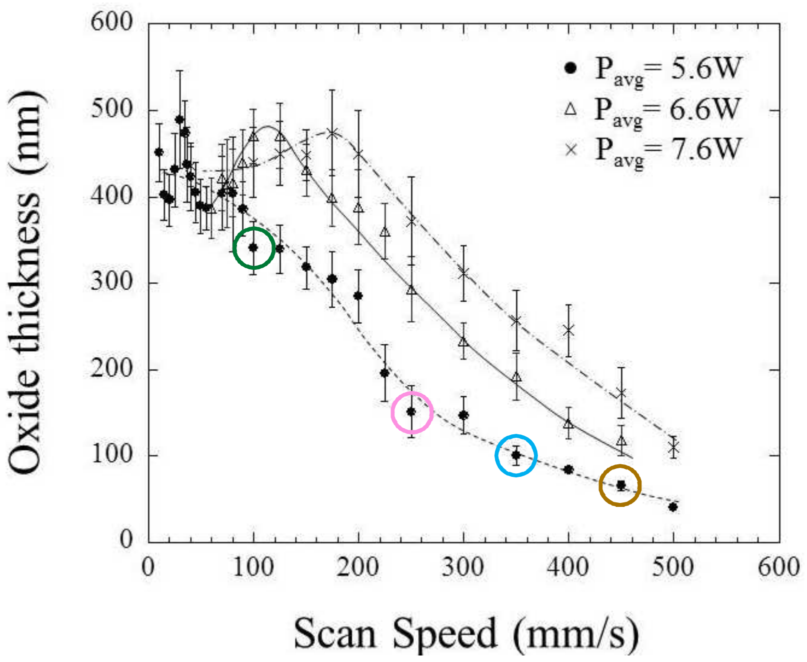


D.P. Adams 2012

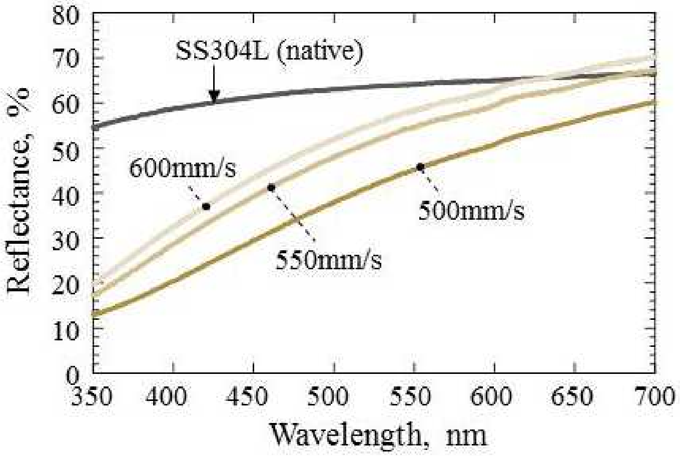
Oxide thickness, in part, determines color.

- Scanning electron microscopy shows oxide layers are ~ 10 - 500 nm.
- Thickness generally increases with fluence or decreasing scan speed (at fixed P_{avg}).

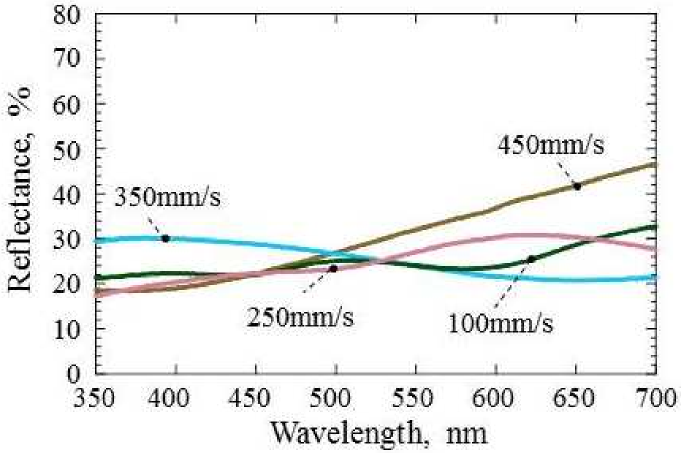
Example: Oxides on Stainless Steel 304L



- For $t_{ox} < \frac{1}{4}\lambda$ of visible light, attenuation.



- For $t_{ox} > \frac{1}{4}\lambda$ of visible light, attenuation and interference.

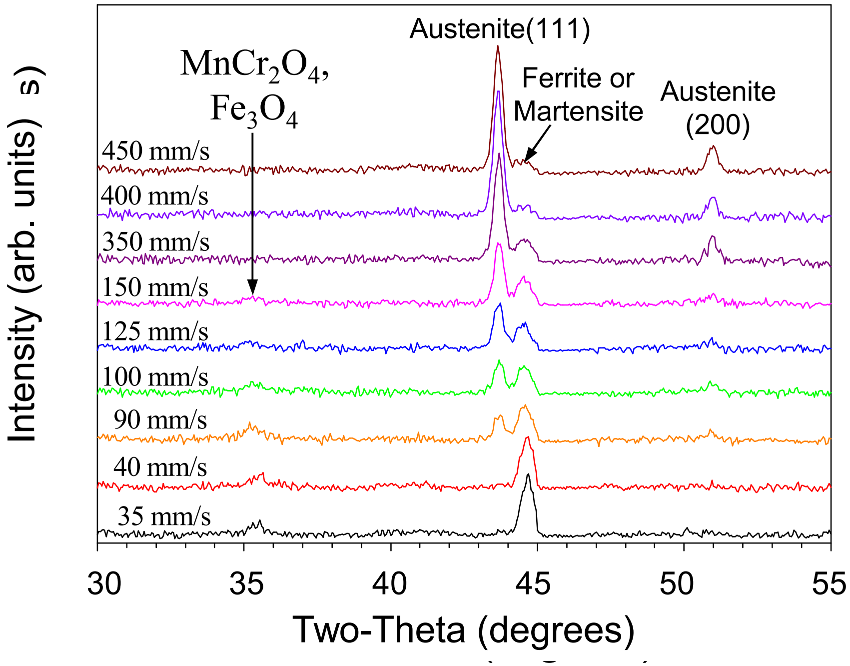


D.P. Adams 2012

Optical constants (n,k) also determine color, and these are affected by phase.

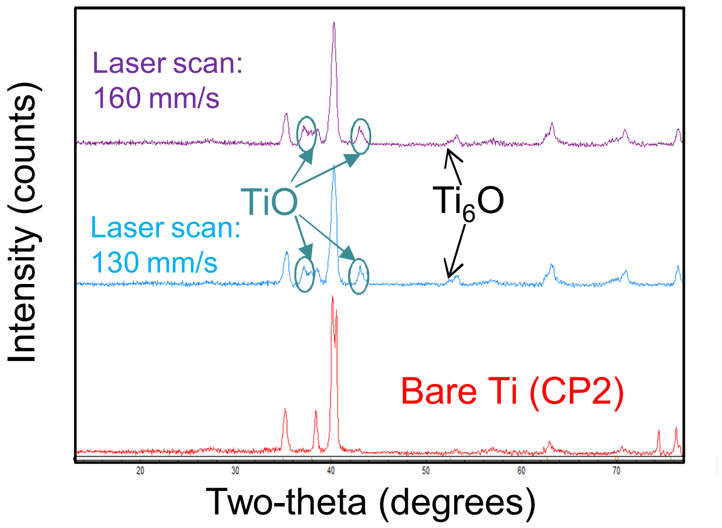
Oxides formed on SS 304L include

- Fe_3O_4 , $MnCr_2O_4$



Oxides formed on Ti include

- TiO (wustite)
- Ti_6O (oxygen intercalation into hex. Ti)

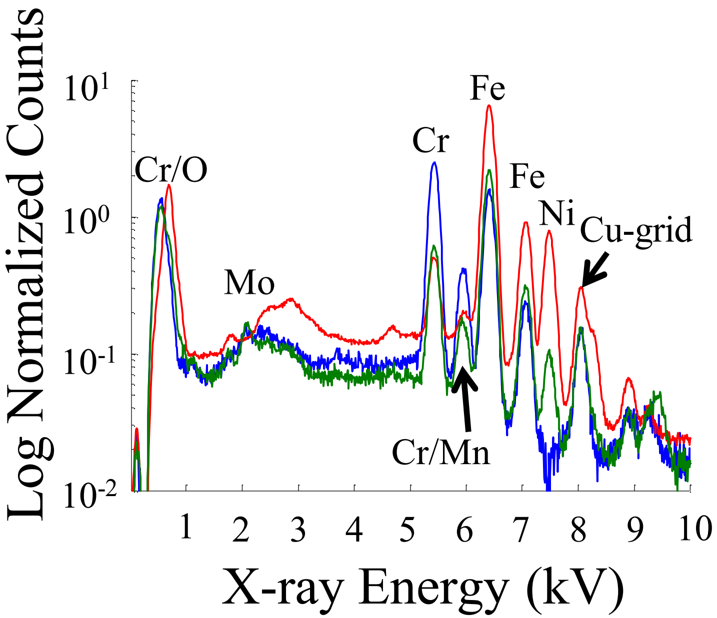


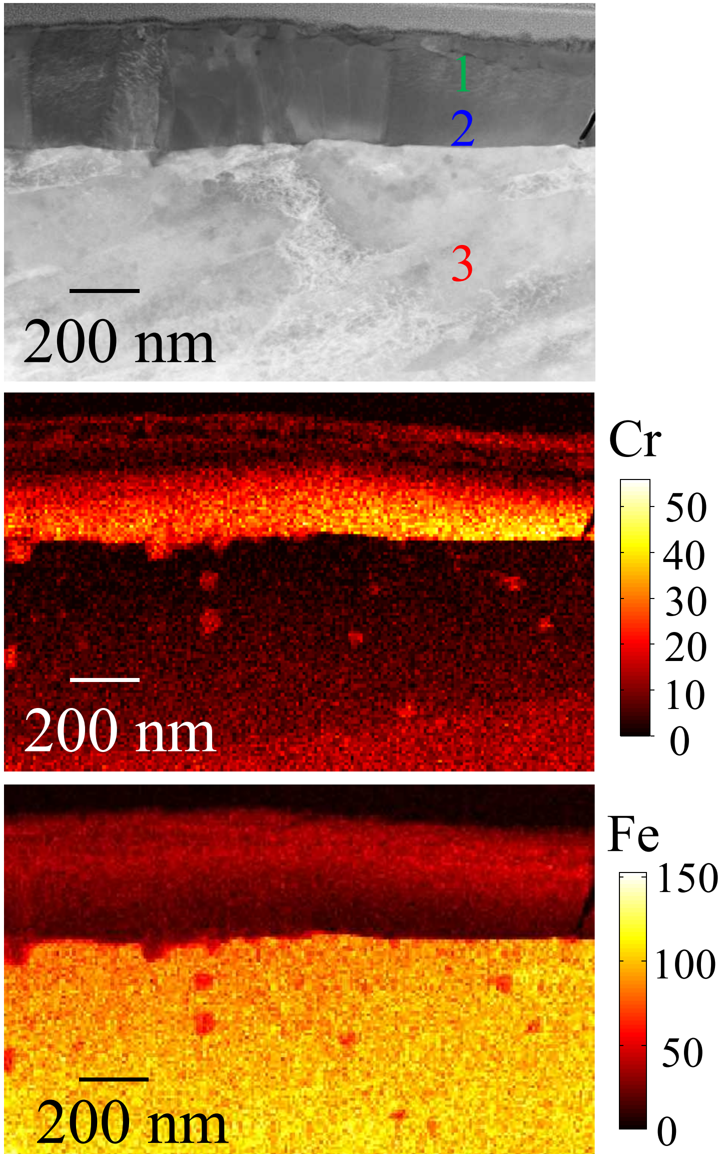
The phase and structure of the substrate is also modified by laser heating.

Optical constants (n,k) also determine color, and these are affected by composition.

Example: Oxides formed on SS 304L are comprised of:

- Compositional gradients through film thickness
- Cr, Mn, Fe, O and trace Ni, Mo





The composition of the substrate is modified due to laser heating.

The mechanical properties of laser-defined oxides have been evaluated.

Oxides defined on SS 304L and Ti have been evaluated using nanoindentation / scratch

- modulus and hardness

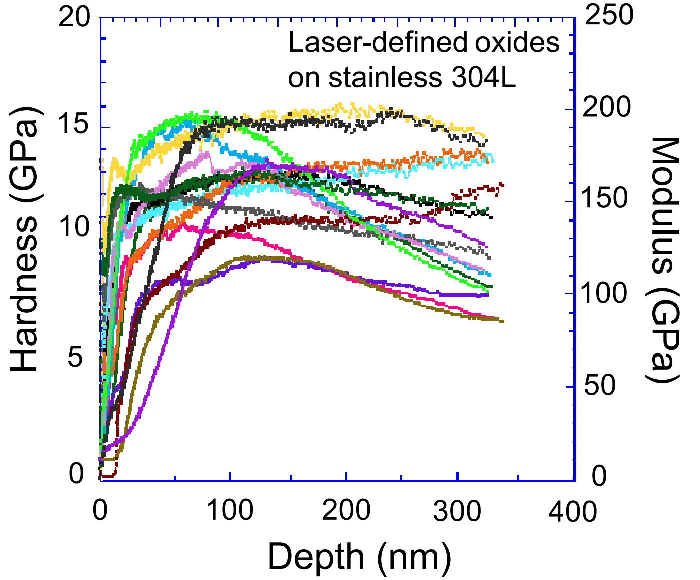
Substrate	E^{ox} (GPa)	H^{ox} (GPa)
SS 304L	137-208	9.5-12.3
Ti (CP2)	199-251	15.1-16.4

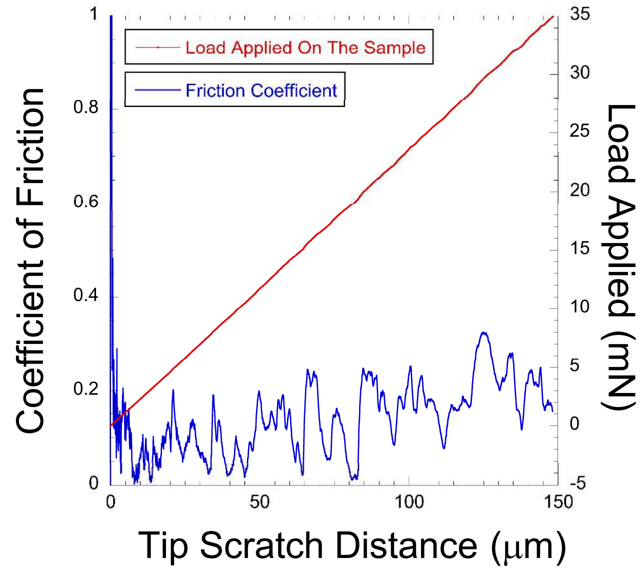
- fracture toughness

Substrate	K^{ox} (MPa $\sqrt{m}$)
SS 304L	2.05-3.2
Ti (CP2)	1.77-2.67

- coefficient of friction

Substrate	C_f
SS 304L	0.15-2.0
Ti (CP2)	0.05-0.09





Technical Objectives for FY12 have been completed

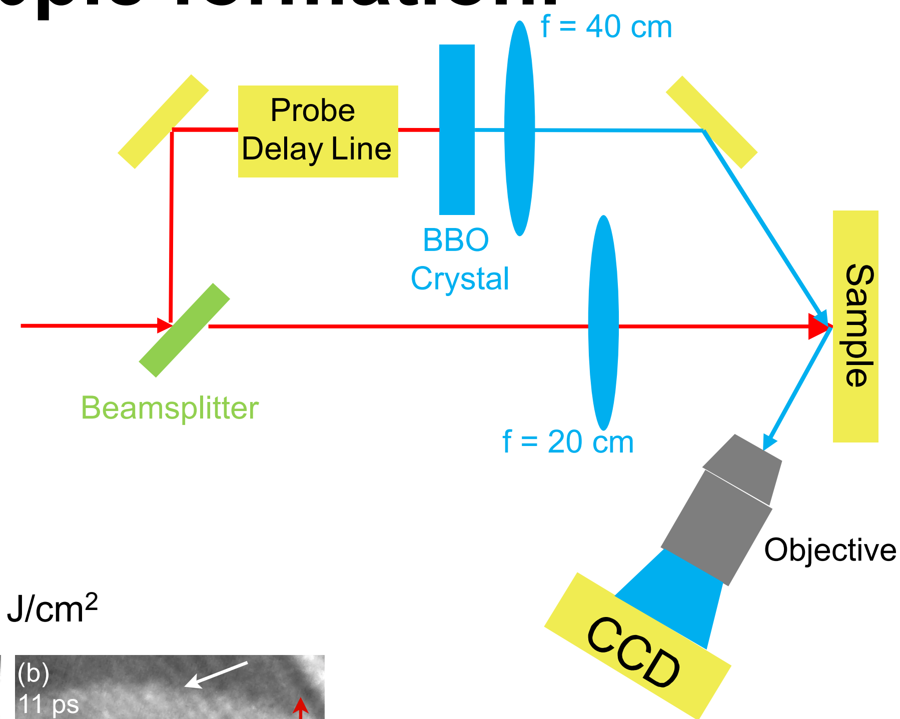
Research includes

- the physical and chemical properties of laser color layers
- micro-color centers forming at selective sites within macro-scale patterns
- the toughness of laser-fabricated color layers
- heat-affected zones via thermal modeling
- feasibility of picosecond and single nanosecond laser coloring of metals
- the temporal evolution of laser-induced periodic structures
- the origin of laser-induced surface ripples
- site-selective formation of periodic surface topographv

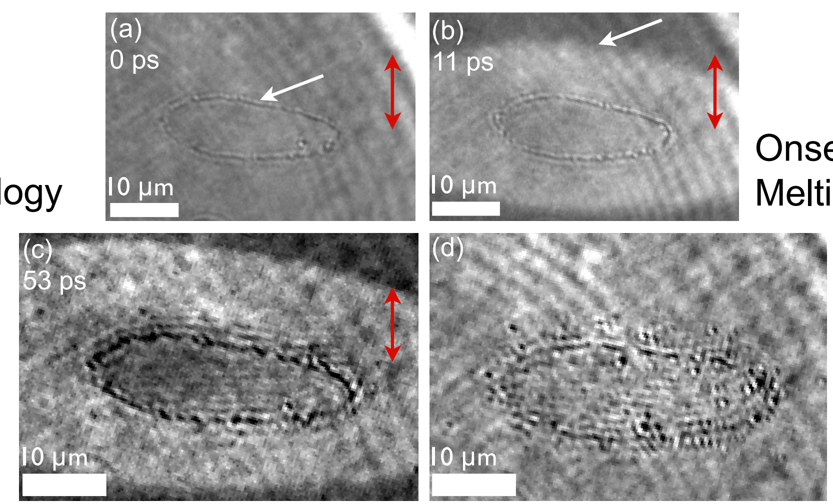
Sandia National Laboratories

In year 2, ultra-fast pump-probe microscopy was used to determine the timescales associated with ripple formation.

- Pump-probe microscope was built, qualified in Y1.
- Experiments involve Si targets
- Long λ (1-2 μm) Laser Induced Periodic Structures (LIPS) form ~ 50 picoseconds after absorption of the pump pulse.



0.34 J/cm^2



Crater created with first pulse creates light-scattering morphology

Onset of surface Melting (with 2nd pulse)

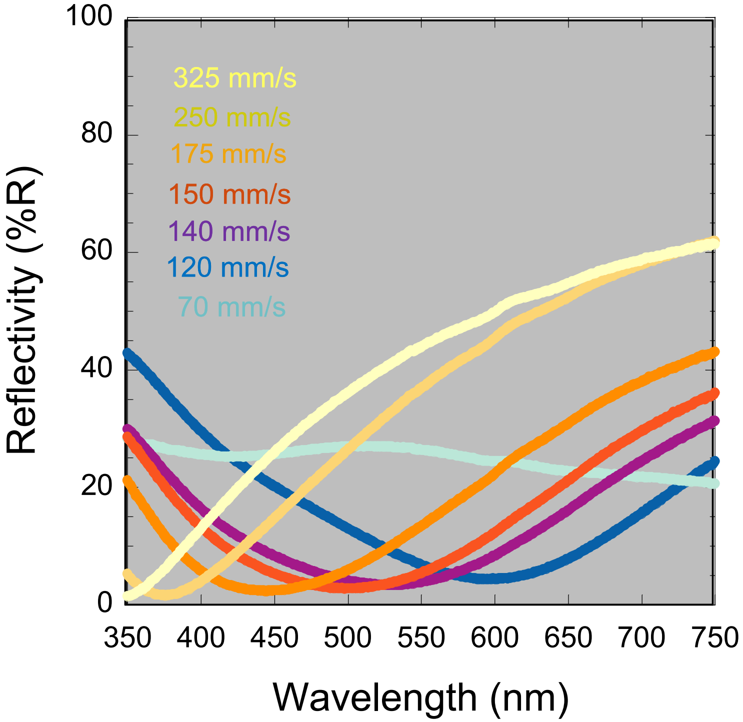
Ripple formation ~ 50 ps

Similar morphology after cooldown

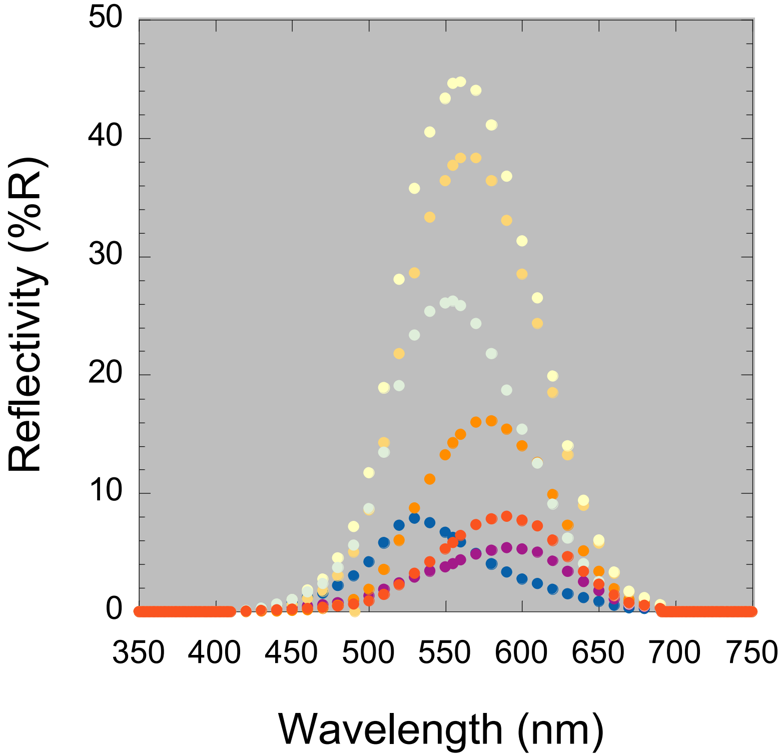
Spectral response as viewed by the typical human eye.

Ex. CP2 grade Ti patterned by 102 ns, 225kHz laser light

Response of unbiased Cary 5000 Spectrophotometer



Corrected according to the luminosity function of the human eye



Color symbols are consistent with appearance to eye

The accumulated fluence largely determines the laser-defined colors.

- Color is similar for a given energy input (J/mm²) – independent of laser scan rate.
- Colors form over a large range of scan rates and for different average powers.
- The color order of gold, orange, red, purple, blue with increasing fluence is the same independent of P_{avg}.