Nondestructive evaluation of incipient corrosion in a metal beneath paint by second-harmonic tomography

Jinpin Ying, Feng Liu, P. P. Ho, and R. R. Alfano

Institute for Ultrafast Spectroscopy and Lasers, Department of Physics, Department of Electrical Engineering, The City College and the Graduate School of the City University of New York, New York, New York 10031

Received April 10, 2000

A second-harmonic optical scanning imaging method for nondestructive evaluation of corrosion of painted metals is demonstrated. Two-dimensional images of the sectional structure from a sample of painted metal with corrosion were obtained by detection of second-harmonic generation (SHG). The second-harmonic signals generated from paint, corrosion, and metal can be spatially imaged in ~10-μm sliced subsurface layers. Corroded metal layers covered with paint are found to have more intensity variation than normal polished metal. The spatial mapping of the second-harmonic signals shows depth differentiation of paint, corrosion, and metal surfaces. The depth of corrosion beneath the paint can be measured from the SHG images.

OCIS codes: 190.0190, 110.6960, 180.5810.

The ability to detect degradation of a metallic surface coated with paint is important in determining whether any deterioration has occurred in aged aircraft, automobiles, boats, or industrial equipment in harsh environments.[1] These surfaces are highly subject to corrosion resulting from moisture or salt penetration through paint or damaged areas of the coating. Periodic repainting of large surface areas such as that of an aircraft is expensive and time consuming. Several nondestructive techniques are commonly used to diagnose whether corrosion has occurred under paint. The techniques include ultrasonic testing,[2] magneto-optic imaging, active thermography, optically aided visual inspection, and speckle correlation.[3] Nondestructive ultrasonic testing based on velocity change, attenuation, and backscattering has been successfully applied by use of laser-induced ultrasonic waves. Magneto-optic imaging[4,5] can image corrosion and cracks over a small area of the magneto-optic crystal plate used in the hand-held scanner. However, it has not been shown conclusively that the magneto-optic imaging technique can detect incipient corrosion that has not yet produced a significant increase in macroscopic surface roughness. Active thermography[4,5] can detect subsurface flaws such as delaminating, debonding, and second-surface corrosion. The initial stages of corrosion do not significantly increase the thermal impedance of the surface compared with that of the layer of paint alone, and detailed resolution of incipient corrosion effects at the top surface requires a very high-speed infrared camera for resolution of surface transients, which might appear only in the few milliseconds after the initial flash-lamp illumination. Visual inspection[4,5] is used to determine the extent of corrosion damage on the skin and around fasteners after the paint has been stripped. As a nondestructive technique for use on painted aircraft, the visual technique is not amenable to detection of chemical changes or microroughness at the paint–metal interface, unless significant corrosion products penetrate the thickness of the paint. At this time there is no method of detecting the early stages of corrosion under paint.

In this Letter we present a novel nonlinear optical method of detecting corrosion beneath paint, using the second-harmonic generation (SHG) signal illuminated from a near-infrared laser to measure the corrosion distribution as a function of focal depth. Two-dimensional (2D) sectional images of the sample were obtained by scanning of the laser source on the y plane and the z depth and mapping the SHG signals. This 2D spatial mapping of the second-harmonic signals showed depth differentiation among paint, corrosion, and metal.

SHG imaging is a nonlinear optical technique that has the potential to image subsurface structures nondestructively.[6,7] The image-forming signal depends on the morphological symmetry and the local matrices of the object. The illumination wavelength used in the technique is in the near-infrared spectral region and provides deeper penetration into the corroded sample than do conventional linear optical approaches using visible light. SHG signals are localized at the focal region as a result of the quadratic dependence on the excitation intensity, leading to optical sectioning without restraint to a confocal pinhole in front of the photodetector.[8,9] The size of the effective region producing SHG may be smaller because of variations in sample composition and structure. Even though the wavelength used is not optimal, the general principle is demonstrated in this Letter.

Backreflection geometry is used to image the surface and subsurface structures in corroded sample covered with a paint coating.[6] A self-mode-locked Ti:sapphire laser system, operating at a center wavelength of 810 nm, with a pulse duration of 120 fs and a pulse repetition rate of 76 MHz, was used to generate SHG from metal samples. The beam was reflected by a dichroic beam splitter and focused onto the specimen by a 20× microscope objective (numerical aperture, 0.4). In the experiment the focal region was approximately 10 μm. Because of the strong nonlinear intensity dependence of SHG signal, only the micrometer-sized focal region can produce the SHG signals. The backscattered SHG light of the sample was collected by the same objective lens, passed through the dichroic beam splitter, and focused by a lens onto a photomultiplier tube (Model R928, Hamamatsu). A computer-controlled lock-in amplifier (Model SR530, Stanford) was used to detect and record the electronic signal from the photomultiplier tube. The main part of emission from the sample is the SHG near 405 nm. The signal was confirmed by use of a narrow-band filter (405DF10, Omega Optical) before the detector. We placed two short bandpass filters (#BG-39, CVI) in front of the photomultiplier tube to block the excitation light. The SHG intensity profile was detected as the focal point and was scanned in and out of the surface by a motorized translation stage. The wavelength of the excited laser was 810 nm. The signal could still be detected from the paint coating and the corroded layer and also reach the uncorroded metal surface. Measuring the spectral transmission of paint, we found that the transmittance percentage from 400 to 800 nm was above 0.03%.

Because of the quadratic dependence of SHG on excitation light, the SHG signal comes mainly from the focal point of the excited laser beam.[9,10] While the focused laser beam was being scanned, the backscattered SHG signal was collected with the same objective and recorded on a computer connected to a lock-in amplifier. The position of the focal point was also provided by the computer-controlled translation stages, which allowed us to locate any point in the layer. By use of a combination of the SHG signal and the spatial information, a 2D or three-dimensional image of the scanning area could be generated.

To demonstrate the principle of SHG mapping for a painted layered structure we used a partly smooth metal surface as a control sample. The control sample was a flat, hand-polished painted surface without corrosion, as shown in the inset of Fig. 1. The paint layer was Scratch-Fix Touch-up (Dupli-color Products Group, SF GM 389). An image of this control sample is shown in Fig. 1 on a log scale. The blue area from $z = 0$ to $z = 25$ μm is the image of the air without the SHG signal. The green area near $z = 40$ μm shows the paint coating covering the surface of metal. Beyond the green area, the blue area from $z = 50$ μm to $z = 160$ μm shows no detected signal. According to our prior knowledge, this area shows the metal sample. The interface between the paint and the metal is quite uniform ($\delta z \sim \pm 10$ μm), as shown by Fig. 1. From the image in Fig. 1, a layer of coating was observed. The thickness of the paint layer was measured to be $\sim$30 μm. The metal interface is clearly shown just underneath the paint layer.

The corrosion samples measured were iron that was exposed to the open air. Owing to the presence of moisture, the corrosion attack penetrated the surface. The inset in Fig. 2 shows a schematic of the corroded surface of the sample without paint. Figure 2 is a log-scale 2D depth SHG image of the sample surface without a paint coating, with the z axis directed into the depth of the metal. The depth of focus was estimated to be $\sim$10 μm. The surface structure of the corroded metal is clearly resolved in the axially scanned direction. The blue part of the image is in air, where no SHG signal is produced. One can easily see that the SHG signal intensity is relatively higher than in the other part of the sample. The green part on the bottom (depth $z = 120$–160 μm) of the image shows the uncorroded metal surface. The red part represents detection of a strong SHG signal from the layer of corroded metal. We obtained good contrast by imaging the layered structure of the corroded metal sample because of the strong intensity variations of the SHG signal for corroded and uncorroded metal. From the 2D imaging map of the sample, the thickness of the corroded layer can also easily be determined. The thickness of the corroded layer is approximately 50 to 120 μm. The depth resolution of the measurement is dependent on the size of the focal point of the excited laser beam. The SHG map also shows the roughness of the surface of the corroded metal with micrometer resolution.

The SHG signal can also be used to detect the corroded metal located beneath a pigmented paint coating. The test structure of the painted sample is shown in the inset of Fig. 3. The SHG depth scan image of the sample structure is shown in Fig. 3 on a log scale. From Fig. 3, the paint coat (the red part in Fig. 3) can be clearly observed when the laser's focal

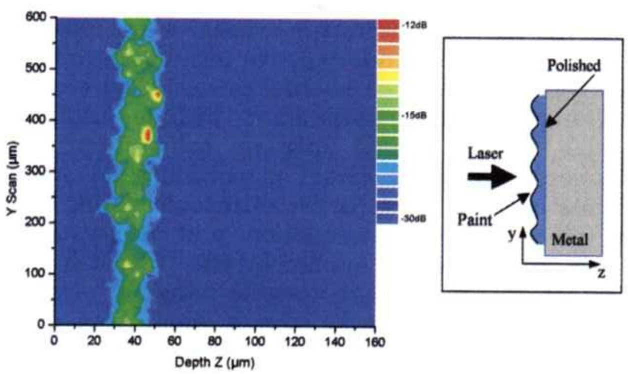

Fig. 1. SHG lateral and axial image for a painted polished metal sample. The inset displays the structure of the metal sample.

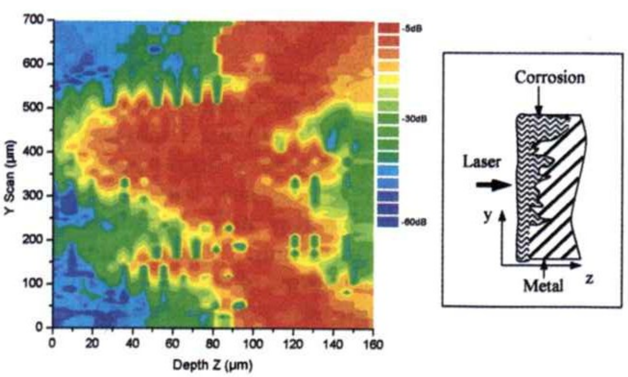

Fig. 2. SHG lateral and axial image of a corroded metal sample without paint. The inset displays the structure of the sample.

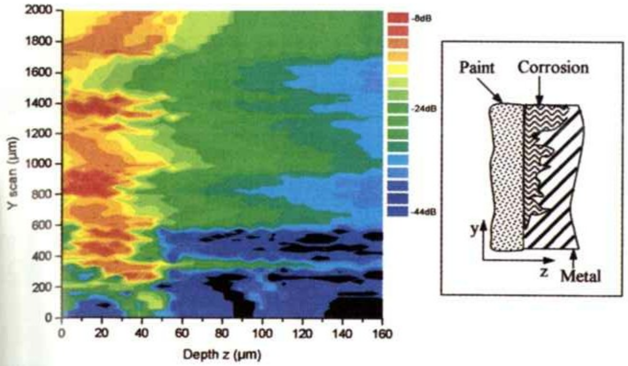

Fig. 3. SHG lateral and axial image of the painted corroded metal sample. The inset displays the structure of the sample.

point axially scans it. The thickness of the paint coat is approximately 30 to 40 μm. Beneath the paint coat, the SHG signal from corrosion can still be found. Owing to attenuation, less laser intensity can reach the corroded metal than the unpainted surface. This difference leads to detection of less SHG signal from the corroded part (see the green part of Fig. 3). The thickness of corrosion is measured to be $\sim$120 μm. It should be noted that, because of the high absorption of the surface paint, the nonuniform thickness of this layer might mask variations in the signal from the corrosion. The pseudocolor display indicates that the paint has the highest (red) SHG signal, followed by corrosion (green), with the weakest (blue) signal for metal and air. The depth probed is $\sim$160 μm. The spatial distribution of the corrosion depth (z) along the surface lateral direction is quite random, varying from $\sim$0 μm (no corrosion) to $\sim$100 μm.

Spatial mapping of the second-harmonic signal from a layered structure showed depth differentiation among paint, corrosion, and metal surfaces. A painted corroded metal surface showed more intensity variation than a normal polished metal sample. The thickness of the corroded metal beneath the paint was measured to within 10-μm accuracy.

The resolution of the SHG imaging method described in this Letter is determined mainly by the laser wavelength and the microscope objective lens. With the current setup using an 810-nm wavelength laser and a 20$\times$ objective lens, the resolution limit of SHG imaging reaches 10 μm. By selection of the proper wavelength in the transmission zone of the paint, metal corrosion can be probed and mapped with better contrast, higher speed, and higher sensitivity, even for thicker painted layers. For example, with 1500-nm light, the attenuation coefficient is only half of the value at 810 nm. The Cr^{4+} cunyite laser offers the potential for development of a portable, high-resolution nondestructive corrosion SHG imaging system.

This work was supported in part by the NASA Institutional Research Awards Program, the Professional Staff Congress of the City University of New York (PSC-CUNY) Research Award Program, and the U.S. Department of Energy Center of Excellence Program.
R. R. Alfano's e-mail address is alfano@scisun.sci.ccny.cuny.edu.

References

1. W. H. Cubberly, ed., *Corrosion*, Vol. 13 of Metals Handbook Series, 9th ed. (American Society for Metals, Metals Park, Ohio, 1987).
2. M. de Billy, F. Cohen-Tenoudji, A. Jungman, and G. J. Quentin, IEEE Trans. Sonics Ultrason. **SU-23,** 356 (1976).
3. T. Frick-Begemann, G. Gulker, K. D. Hinsch, and K. Wolff, Appl. Opt. **38,** 5948 (1999).
4. D. J. Hagemaier, A. H. Wendelbo, and Y. Bar-Cohen, Mater. Eval. **43,** 426 (1985).
5. M. Fontana, *Corrosion Engineering* (McGraw-Hill, New York, 1986).
6. Y. Guo, P. P. Ho, H. Savage, D. Harris, P. Sacks, S. Schantz, F. Liu, N. Zhadin, and R. R. Alfano, Opt. Lett. **22,** 1323 (1997).
7. Y. R. Shen, *Principles of Nonlinear Optics* (Wiley, New York, 1984), Chap. 25.
8. S. Fine and W. P. Hansen, Appl. Opt. **10,** 2350 (1971).
9. W. Denk, J. H. Strickler, and W. W. Webb, Science **248,** 73 (1990).
10. J. Ying, F. Liu, and R. R. Alfano, Appl. Opt. **38,** 224 (1999).