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Ultrasonic Nondestructive Imaging of Worn-Off Hallmarks on Silver: Preliminary Results

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Technical Report Abstract Page

Title	Ultrasonic Nondestructive Imaging of Worn-Off Hallmarks on Silver: Preliminary Results		
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Hallmarks on silver objects can reveal much about the history of the piece. The name of the silversmith, the date of manufacture, the quality of the metal alloy, and other information can be determined from study of the hallmarks. Because silver requires polishing to maintain its lustrous metallic surface, hallmarks tend to be polished away over time, resulting in the loss of important historical information. By utilizing scanning acoustic microscopy (SAM), an image of these vanished or illegible marks can be recovered. Three ultrasonic imaging modes are presented: time resolved surface wave imaging of the near surface deformation in the silver, direct reflection images of the surface relief, and direct reflection from the silver back surface through the remnant deformed silver. The contrast in these images is caused by variations in the ultrasonic velocities in the silver, density changes, and acoustic attenuation due to the deformed silver microstructure. This technique is non-destructive, non-contact, and does not require a sample to be taken from the object.

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Introduction

The use of hallmarks on silver has a long history, dating back to at least the sixth century AD. A series or system of five marks has been found on Byzantine silver dating from this period, though interpretation of these marks is still not completely solved [1]. Hallmarking of European silver probably originated in France in the thirteenth century and spread from there to other countries. The French standard for silver quality was established in 1260, the first use of a town mark was established in 1275, the individual maker's mark was introduced in 1355, and the date letter system introduced in 1427. In England, the silver standard mark was established in 1300 followed by the introduction of a maker's mark in 1363, the town mark in 1423 and the date letter mark in 1478 [2]. As the history and standards of hallmarking silver and gold objects from various countries is complex, it should be consulted on an individual basis (See Figure 1).

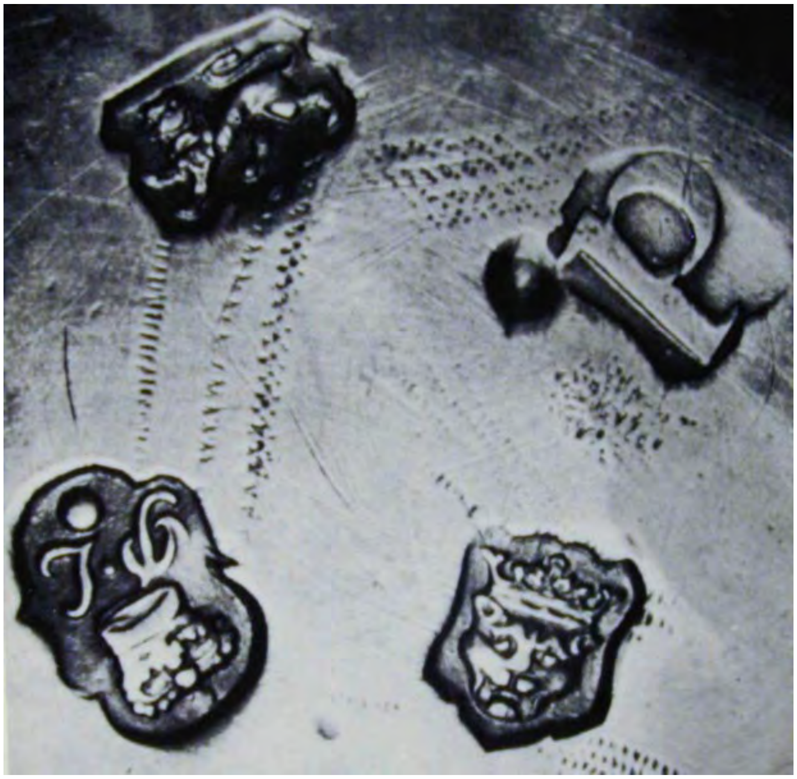


Figure 1: Typical set of English hallmarks indicating that the object is made of sterling silver and made by Paul Lamerie in London in the year 1739.

Hallmarks on silver and gold objects can fix these pieces in history by providing direct evidence of the maker, the place and date of manufacture, and the quality of the metal alloy at a particular time. To some extent then the historic, monetary, and intrinsic values of the objects are directly linked to the ability to read the hallmarks. Silver's propensity to tarnish means that it must to be polished regularly to maintain its desired bright metallic surface finish. The polishing process removes a thin layer of silver metal so that over time the hallmarks will be gradually reduced to the point where they are either illegible or completely polished away, resulting in the loss of valuable historic information. The ability to read the original marks would greatly aid in the placement of the object back into its rightful place in history.

Even though the hallmark can be completely worn away, there may still be sufficient residual plastic deformation within the metal from the act of striking the surface to create the hallmark. This residual deformation can be characterized in the form of an acoustic response when the surface is insonified with a focused acoustic beam; the amplitude of the response is then used to create an image on a CRT screen. The highly polished, i.e., smooth, silver surface provides a nearly ideal medium for the utilization of scanning acoustic microscopy imaging techniques.

Ultrasonic Imaging Systems and Scanning Acoustic Microscopes

The ultrasonic imaging technologies for visualizing the surfaces and interiors of opaque solids are well established [3]. Between 1929 and 1931, Sokolov and Mulhauser independently proposed the use of ultrasonic waves to form images of the interior of materials for materials characterization and nondestructive evaluation (NDE). During the 1930s all efforts to develop ultrasonic images involved the development of acoustic amplitude sensitive screens that displayed visible contrast in proportion to the acoustic amplitude incident on the screen. These image converter screens (such as the Pohlmann Cell and the Sokolov Tube) had such poor sensitivity and resolution that little use was made of them other than as curiosities. Pulse-echo and pulse-transmission C-Scan images, using both focused and unfocused ultrasonic beams, were introduced in the early 1950s. The primary use was for industrial NDE. These initial C-Scan images were displayed on photographic or voltage sensitive paper and were acquired by scanning a single transducer back and forth over the subject material. The image was built up line by line. By the early 1970s ultrasonic C-Scan inspections of both the surfaces and interior volumes of industrial materials were in general use and C-Scan images had been produced as high as 50 MHz in frequency. In the early 1970s work at Stanford University under the direction of C.F. Quate [4] combined zinc oxide on sapphire transducers, C-Scan data acquisition, and microwave electronics to create very small ultrasonic images at GHz frequencies. These images rivaled optical microscopy in resolution, detail, and field of view; therefore, the devices that made them were called Scanning Acoustic Microscopes. The GHz frequencies, low depths of penetration, and very small fields of view limited the industrial usefulness of scanning acoustic microscopy, except for microelectronic assemblies. However, the near-optical resolution of the acoustic microscope images provided a new emphasis and enthusiasm for ultrasonic imaging in general. This renewed effort, combined with the collateral advances in the power, storage, and display capabilities of small computers, resulted in three decades of rapid progress in ultrasonic imaging devices, methods, and applications. By the start of the 21st century, ultrasonic imaging methods were well established to characterize material microstructures, bonds, defects (flaws, voids, cracking, porosity, layer delaminations), coating delaminations, elastic modulus and density variations, heat affected zones in welds and other fusion processes, stress distributions in isotropic materials, and in vitro carious lesions. Materials examined include ceramics, composites, glass, metals and alloys, polymers, plastics, semiconductors, electronic components, geological materials, coffee and soybeans, bone, teeth, soft biological tissue, and organic compounds. However, a literature search has found only three references to acoustic microscopy and metal or ceramic art objects [5,6,7].

Several texts are available that clearly describe ultrasonic imaging and acoustic microscopy [3,4,8]; therefore, the characteristics and operation of the systems will only be summarized here. A typical transducer used for acoustic imaging consists of a piezoelectric layer cut to a specified frequency and bonded to a plano-concave lens to focus the ultrasonic beam. For high-frequency operation, the lens is usually fabricated from single crystal sapphire or fused quartz. Alternatively, eliminating the lens and spherically curving the piezoelectric layer itself can also focus the ultrasonic beam. In the case of pulse-echo C-Scan data acquisition, the transducer acts as both the transmitter and receiver of the acoustic energy. A short electrical pulse is applied to the piezoelectric layer to create the acoustic pulse, and return acoustic echoes interact with the layer to create electrical signals. The object to be scanned is placed at the focal point of the ultrasonic beam. What makes an acoustic microscope unique is the ability to place the focal point of the acoustic energy either on the surface of the object or subsurface in the object's interior. Again, as with all C-Scan type data acquisition, the image is acquired by raster scanning the ultrasonic beam and acquiring echo amplitudes at an increment along the scan lines equal to the line-to-line spacing (See Figure 2).

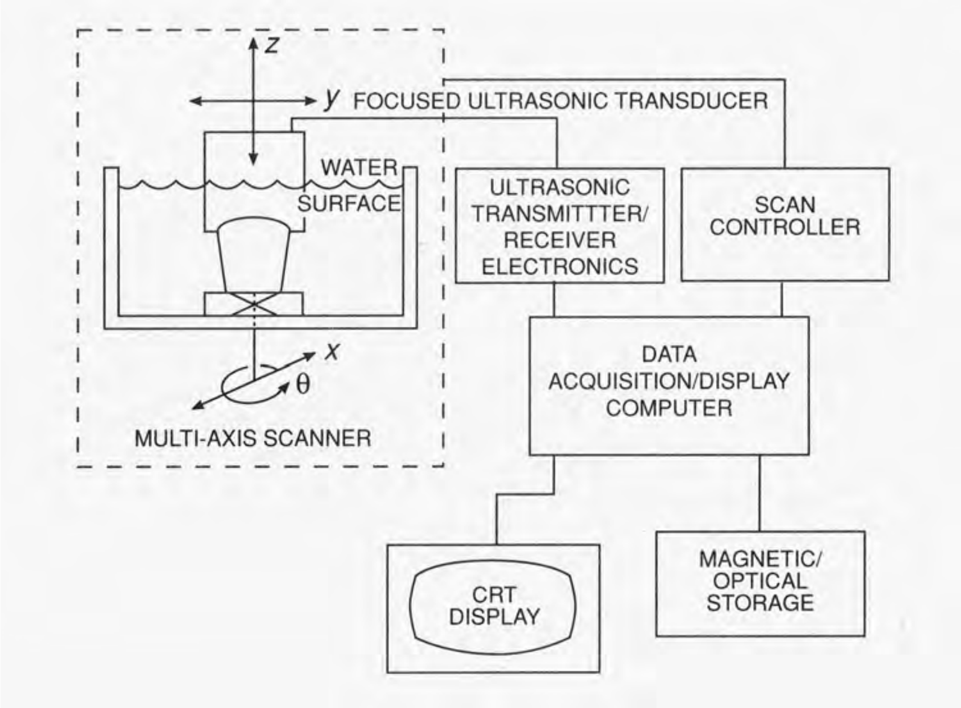
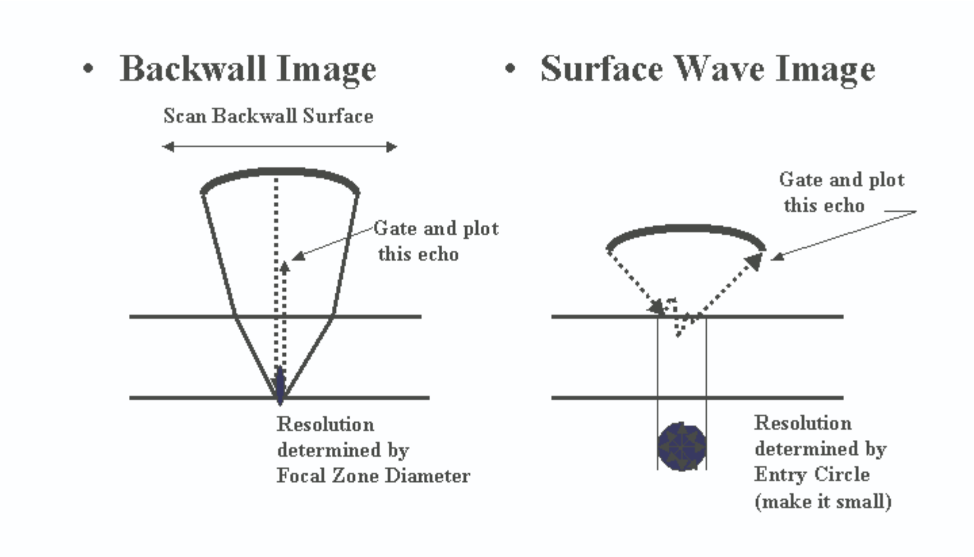


Figure 2: Schematic of an ultrasonic imaging system; higher frequencies and higher image magnification would make the same schematic an acoustic microscope.

For frequencies much above 1 MHz, acoustic waves are rapidly attenuated in air so it is necessary to utilize a coupling fluid between the transducer and object to be imaged. The acoustic properties of the coupling fluid are a significant factor in determining the resolution that can be achieved by the acoustic imaging system. The most used fluid is water but other fluids have acoustic properties (namely a higher or lower velocity) that make them superior to water, particularly when surface wave imaging is used. For this work FC-40 (an inert fluorocarbon fluid with a velocity less than half that of water) was used to make surface wave images in the sterling silver objects discussed here. Usually, the object is submerged in the fluid while being scanned, but some systems use pumped water columns essentially squirted at the surface being scanned. The images acquired in this work were all made by immersing the silver objects in FC-40 or water.

The contrast changes in acoustic images are produced by variations of elasticity, density, and acoustic attenuation within the material to be imaged. In the specific case of imaging worn hallmarks, this paper will demonstrate that images of the residual deformation in the metal from the stamping process can be obtained by two of the three ultrasonic imaging modes mentioned in the abstract: (1) Surface wave imaging of the surface containing the hallmark deformation (See Figure 3a), (2) Back-wall or back surface imaging where an acoustic beam is focused through the full thickness of the silver and on the back surface containing the hallmark deformation (See Figure 3b). In other words, surface waves are used to produce images of the entry surface, i.e. the struck surface, where back-wall images are obtained from the surface opposite to the struck surface.



(a) (b)

Figure 3: Schematic showing (a) back surface reflection imaging (or back-wall imaging) and (b) mode converted surface wave imaging.

Experimental Results

A first step in determining if residual deformation in silver or any other material is a candidate for acoustic imaging is to determine the stability of this deformation over time. The lowest temperature that might affect this stability is the residual stress annealing temperature. This is generally considered to be approximately 4/10 (0.4) of the absolute melting temperature as expressed in Kelvins (K). The highest temperature below the melting point affecting the retention of the deformation is less exact, but is the range in temperature at which recrystallization occurs. Here the grain boundaries in the silver migrate and the microstructure entirely recrystallizes. Any residual plastic flow remaining from a hallmark would begin to relax at the stress anneal and could totally disappear during recrystallization. Since the melting point (Mp) of sterling silver is 893 ºC = 1166 K, the stress anneal would fall at approximately 0.4 × 1166 = 466 K or approximately 93 ºC above the boiling point of water (100ºC or 373 K). Room temperature is typically approximated at 300 K and ambient temperature in the middle latitudes is between –40 ºC and 54 ºC (233 K and 327 K). Since the lowest critical temperature for sterling silver (466 K) is well above these temperatures, it seems reasonable to expect the residual deformation produced by a hallmark stamp to be relatively stable over a few hundred years of time, even if repeatedly washed in hot water.

A second consideration in imaging residual deformation is to determine the acoustic properties of the subject material and any possible anisotropy of the material. Unless the deformation process produces microfractures, there is no reason to anticipate that a truly isotropic material would be rendered anisotropic by plastic deformation. Anisotropic materials, however, should undergo considerable change during deformation, since a local deformation would significantly rearrange that microstructure. It seemed appropriate to estimate the anisotropy in silver to determine if ultrasonic backscatter from the silver microstructure itself might be used to track the deformation underlying hallmarks. The three elastic constants for single crystal silver (cubic system) are [10]: C11 = 1.239 Mbar, C12 = 0.939 Mbar, and C44 = 0.461 Mbar. Isotropic materials have only two independent elastic constants instead of the three required to describe the cubic system. A typical test for isotropy (again within the cubic system) is the equality of [C11 – C12] / 2.0 to C44. Clearly 1.239 – 0.939 / 2.0 = 0.150 and is not equal to 0.461, so silver possesses considerable anisotropy. Therefore ultrasonic backscatter from the silver grains should be able to track the modifications in the microstructure caused by the plastic flow in the silver around the hallmarks. Having established this possibility, one should immediately state that backscatter imaging of the silver microstructure has not proven effective to date for displaying residual deformation in the silver. Sterling silver proved to have a longitudinal velocity of 3.89 mm/microsecond, a transverse velocity of 1.73 mm/microsecond, and a surface wave velocity of 1.63 mm/microsecond.

Sterling Silver Coupons

Initial experimentation was conducted on two blank sterling silver (92.5% silver) coupons measuring approximately 25 mm × 25 mm × 3 mm. An experienced silversmith then placed three different hallmarks on one surface. A silversmith was employed to produce the hallmarks, thinking that he would strike the silver with approximately the same force used by silversmiths for the past several hundred years so that the marks would be neither too deep nor too shallow. Approximately 0.075 mm was removed from the struck surface of one of the coupons with a rotary lapping machine. This was done to approximate the slow removal of the silver surface in much the same manner as years of polishing. The struck surface of the second coupon was polished in the same manner until essentially all of the hallmarks were removed. Once the marks were completely removed from the surface, the coupon was placed in a container with some keys, and the container was vibrated to produce scratches on the silver to simulate the surface on a genuine aged art object. The three ultrasonic images shown in Figure 4 illustrate the detail ultrasonic imaging can produce on both intact hallmarks and the deformation remaining after removal by polishing. Figure 4a shows a 50 MHz F/2 back wall image of a coupon that still retains almost all of the hallmarks placed on it. Figure 4b shows a 50 MHz F/2 back-wall image of the residual deformation in a similar coupon where almost all of the original hallmarks have been polished away. Figure 4c shows a 20 MHz F/1 surface wave image of the same deformation in 4b except viewed from the surface containing the residual deformation. Both back-wall images were acquired using water to couple the ultrasonic beam into the part. The surface wave image used FC-40 to mode convert a longitudinal wave in the fluid into a surface wave on the silver coupon's surface.

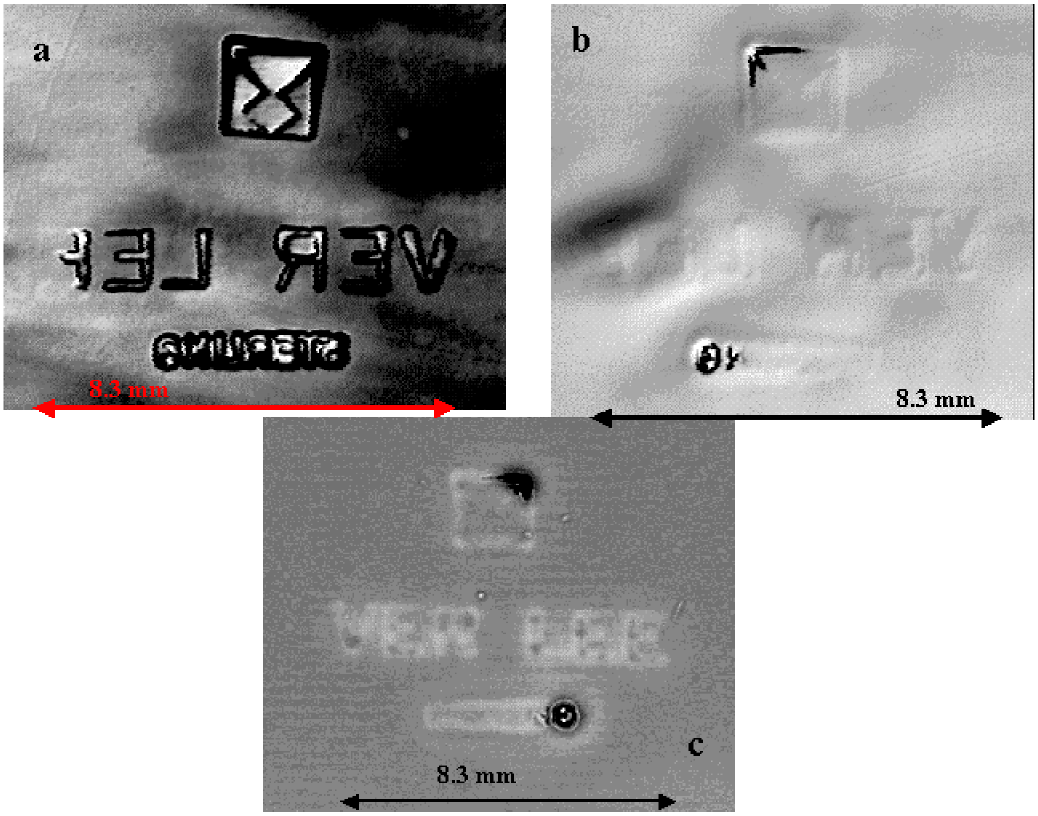


Figure 4: Three ultrasonic images of the sterling silver coupons. (a) A 50 MHz F/2 back-wall image of the original hallmark. (b) A 50 MHz F/2 back-wall image of the residual deformation remaining in a similar coupon where the hallmark has been polished away. (c) A 20 MHz F/1 surface wave image of the same deformation shown in 4b, except imaged from the surface containing the deformation (a surface wave image).

Sterling Silver Spoon Handle

Figure 5 shows a set of surface wave images of a sterling silver spoon wrought by Peter and Ann Bateman dating from 1792. This teaspoon, one from a set of eight, was chosen because its four hallmarks varied from perfectly readable to completely polished away. Also, the four hallmarks are legible on the other spoons from this set, making it easier to target the desired image quality. In Figure 5a the makers' initials are clear but much of the remaining hallmarks have been removed or were improperly struck. Figure 5b shows the isolation, magnification, and partial recovery of one of the hallmarks believed to be that of a lion. The image of the "lion" shown in Figure 5c is the best result of a series of trials where the focus of the transducer was changed slightly for each trial. The importance of even very small changes in the system focus has been repeatedly demonstrated in the course of this work.

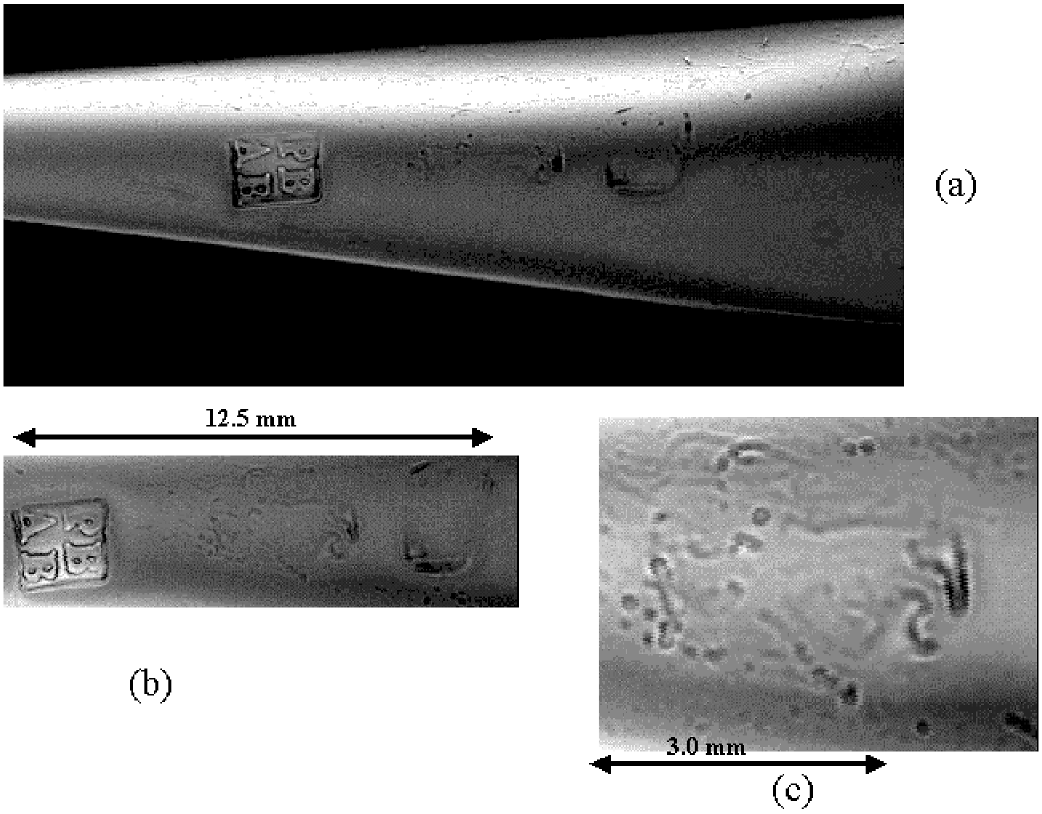


Figure 5: Ultrasonic images of the handle of a sterling silver spoon wrought by Peter and Ann Bateman dating from 1792. The initials of the makers are clear but much of the remaining hallmarks have been removed or were improperly struck; (c) shows the isolation, magnification, and partial recovery of a figure thought to be a lion.

Knife Blades: Sterling silver fish knife blade and steel table knife blade

Figures 6 and 7 are intended to show the lack of subsurface deformation where one would naturally assume that it should be present. Figure 6 shows a set of ultrasonic back-wall images of the sterling silver blade of a French fish knife dated approximately1875 to 1925. One hallmark has been isolated and magnified (b) for comparison to the back-wall image of the deformation in the test coupon (c). Clearly no deformation appears to extend from the fish knife hallmark, suggesting that it has either been improperly struck by the silversmith or the residual deformation has been ‘relaxed’ during an annealing process. Some French hallmarks were actually applied to the roughed-out silver sheet before the object was completed. The finished object would have been subjected to multiple annealing steps during its manufacture, thereby relieving the metal of any residual deformation from the hallmarking procedure. This is in comparison to the English system of applying the hallmarks only after the object had been completed; thus the residual plastic deformation in the metal would be retained. It is also possible that the heat from the process of soldering the handle to the blade was sufficient to cause a localized annealing of the hallmarks since they are placed quite close to the attached handle.

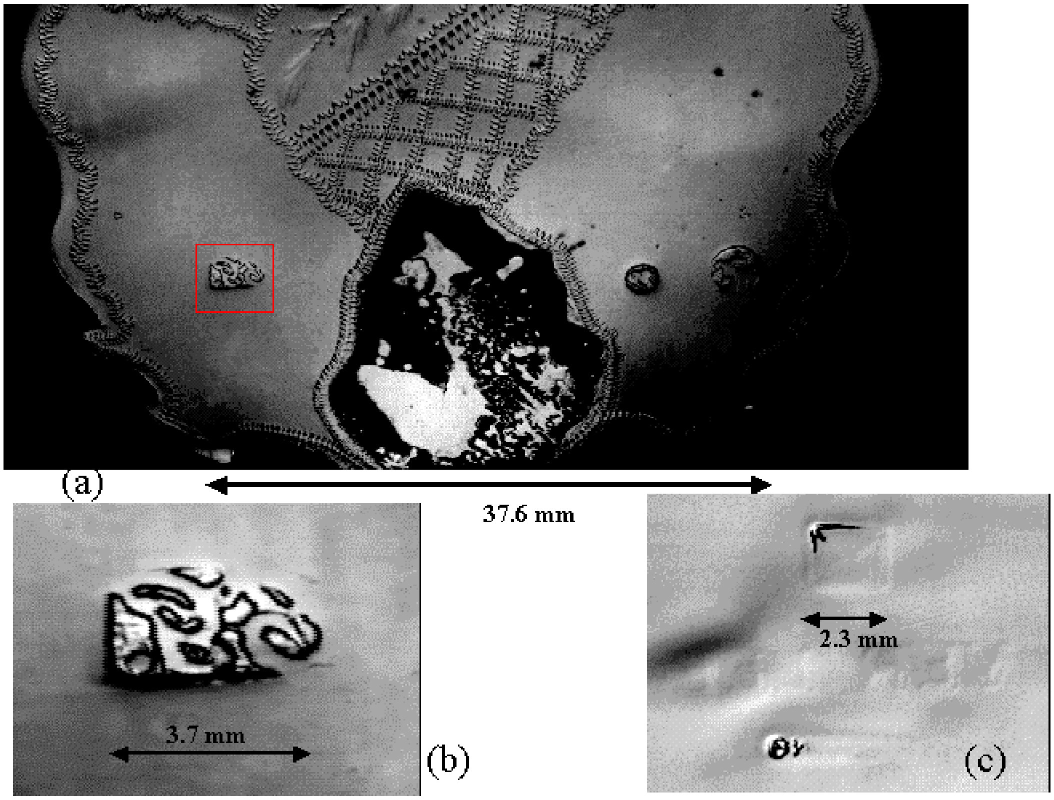
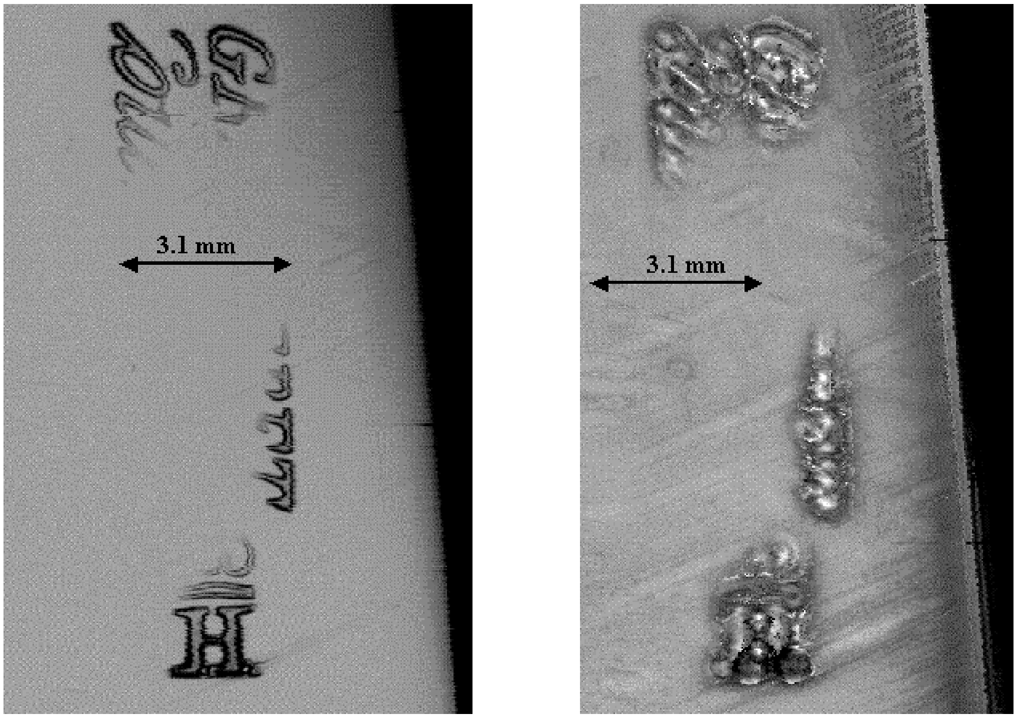


Figure 6: Ultrasonic back-wall image of the sterling silver blade of a French fish knife dated approximately 1875 to 1925. One hallmark is isolated and magnified for comparison to the back-wall image of the coupon. No deformation appears to extend from the fish knife hallmark, suggesting that it is (1) incomplete, (2) improperly struck, (3) unstable over 100 years of the temperature environment it encountered, or (4) an annealing process has removed the residual deformation.

Figure 7 shows a direct reflection image (a) and a surface wave image (b) of the steel blade of a French table knife dating from the early nineteenth century. Again, no deformation is observed in the blade surface where the writing has been polished or ground away. This suggests an incomplete original impression or possibly that etching was used to produce the characters on the blade.



(a) (b)

Figure 7: (a) A direct reflection image and (b) a surface wave image of the steel blade of a table knife. Deformation is not observed in the blade surface where the writing has been polished or ground away, suggesting a poor original impression or, possibly, that etching produced the inscription.

Conclusions and suggested further work

At this point there are several confusing aspects of this work. Results from the modern sterling silver blanks have been very encouraging. The hallmarks were placed on the blanks in the early summer of 1997 by an experienced silversmith. These hallmarks were well and truly struck (i.e., their original existence is well documented). After the hallmarks were removed by polishing, ultrasonic imaging produced clearly decipherable images of the remnant deformation on the surface of the silver. Both surface wave imaging and back-wall imaging were clearly effective at displaying residual deformation in the silver. Where only part of the hallmark was removed, the imaging methods are able to show remnant deformation extending out from the remnant surface dents in the surface. The blanks are now approaching four years in age. Repeat images show results in 2001 that reproduce the results shown in the initial 1998 images. However, despite the clear anisotropy in silver, backscatter imaging of the silver microstructure has not yet proven effective. Neither the silver microstructure itself nor deformation of that microstructure has been shown by backscatter imaging at the 20 MHz or 50 MHz frequencies used to date. The failure of the backscatter imaging is confusing since both the back-surface reflection images and the surface wave images clearly indicate that the acoustic properties of the silver showed significant changes at the hallmark locations.

Work to recover partially obliterated hallmarks on antique silver objects has been less encouraging than the work on the coupons. But in these cases one cannot be certain that the hallmarks were properly struck in their original condition. The silver blade of the French fish knife (See Figure 6) demonstrates this case in point, as does the steel blade of the table knife (See Figure 7). The fish knife is ideally configured for back-wall imaging and yet no remnant deformation could be shown to extend from the dented marks remaining on the blade. Were these hallmarks ever more extensive or is the deformation in the French silver composition unstable over a time period of 200 years. Similar results were obtained for the surface wave images on the steel blade of the table knife. No residual deformation was shown extending from the dented patterns on the blade surface.

Surface wave images of antique coins suggest that downward or compressive deformation (i.e., a dent) is more readily defined than the upwelling of material. Efforts to image the originally upraised patterns of the years in which coins were struck have not yet been successful. This suggests that the deformation under dents is more readily detected than bulges.

Clearly, considerable work is required to resolve the issues this preliminary study has raised.

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References

[1] Dodd E C, Byzantine Silver Stamps, *Dunbarton Oaks Studies*, vol 7, 1961.

[2] *Touching Gold and Silver: 500 Years of Hallmarks*, Catalog of an exhibition at Goldsmith’s Hall, Foster Lane, London EC2, November 7-30, 1978.

[3] Gilmore R, Industrial Ultrasonic Imaging/Microscopy, in Papadakis E (ed), *Physical Acoustics*, Volume XXIV, New York, Academic Press, 1999, pp 275-346.

[4] Lemons R and Quate C, Acoustic Microscopy, in Mason, W P and Thurston R N (eds), *Physical Acoustics*, Volume XIV, New York, Academic Press, 1979, pp 1-92.

[5] Stavroudis, Chris, *Possible Applications of Acoustic Emission and Scanning Acoustic Microscopy to the Field of Art Conservation: Phase I- Preliminary Report - Final Draft*, Malibu, California, Getty Conservation Institute, 1989, pp 43-61.

[6] Benson P L, *Scanning Acoustic Microscopy and Potential Application in Archaeological Conservation*, dissertation in partial fulfillment of the requirements for the Degree in Conservation, Institute of Archaeology, University of London, 1991 (unpublished).

[7] Ouahman R et al, Application de la Microscopie Acoustique a l'Etude des Produits de Corrosion du Fer Archeologique, *Metal 95: Proceedings of the International Conference on Metals Conservation, Semur en Auxois, France, September 25-28, 1995*, (1995) pp 50-54.

[8] Briggs Andrew, *Acoustic Microscopy*, Oxford, Oxford University Press, 1982.

[9] Simmons G and Wang H, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, Cambridge, MA, MIT Press, 1971, pp 85-86.

Materials

FC-40 Fluorinert Brand Electronic Liquid: a perfluoro liquid containing no hydrogen or chloride: 3M Specialty Materials, 3M Center, St. Paul, Minnesota 55144-1000 USA, Tel.: 651-737-6501.

Résumé

Les poinçons sur les objets en argent peuvent apprendre beaucoup de choses sur l'histoire de la pièce. Le nom de l'orfèvre, la date de fabrication, la qualité de l'alliage, ainsi que bien d'autres renseignements, peuvent être tirés de l'étude du poinçon. Comme l'argent demande à être astique pour garder son brillant, avec le temps, les poinçons ont tendance à s'estomper, ce qui entraîne la perte d'importants renseignements historiques. En utilisant le Microscope à Balayage Acoustique, on peut retrouver une image de ces marques effacées ou illisibles. Plusieurs types d'images peuvent être obtenues: image par balayage montrant la déformation superficielle de l'argent, images en réflexion directe du relief de la surface, images en réflexion directe de l'envers de l'objet grâce à ce qui reste d'argent déformé. Le contraste dans ces images est dû aux différences de vitesses ultrasoniques au sein de l'argent, aux variations de densité et à l'attenuation acoustique dûe à la déformation de la microstructure de l'argent. Cette technique est non destructive, ne nécessite aucun contact et ne demande pas qu'un échantillon soit prélevé sur l'objet.

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