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Combined THz and LIPS analysis of corroded archaeological bronzes☆

I. Cacciari, J. Agresti, S. Siano

Istituto di Fisica Applicata "Nello Carrara" — Consiglio Nazionale delle Ricerche, Via Madonna del Piano 10, 50019 Sesto Fiorentino, FI, Italy

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ABSTRACT

In this work we have studied corroded archaeological artefacts by combining THz and laser induced plasma spectroscopy (LIPS). The main aim of the work was the assessment of the potential of the THz TDS reflectometry for achieving stratigraphic information and the presence of the metal bulk beneath encrustations and alteration layers before measuring LIPS elemental depth profiles. The behaviour of the reflected THz pulses was formerly investigated by preparing a set of suitable mock-ups, then measurements were carried out on a set of authentic archaeological samples exhibiting different stratigraphic situations, and eventually a deeply corroded Egyptian bronze figurine was characterised. The results achieved show the range of stratigraphic information, which can be provided by THz and the advantages of the present analytical combination.

1. Introduction

Archaeological bronzes typically present stratified earthy concretions and corrosion compounds. The latter often include reddish Cu(I) (cuprite) and/or blackish Cu(II) (tenorite) oxides with dispersed nantokite in close proximity of the metal substrate, along with Cu-carbonates, Cu-sulphates, and Cu-hydrochlorides at the outer layers, which produces the characteristic greenish appearance. The thicknesses of these mineral layers determine the overall degree of corrosion of archaeological copper alloys, which can be very variable, ranging from pseudomorphic oxidation with minimal alteration of the original surface to the destruction of the latter and the complete mineralisation of the metal walls [1].

The characterisation of the state of conservation of a given metal artefact has a crucial importance whenever approaching the analysis of its alloys using non-destructive techniques such as X-ray fluorescence (XRF) and Particle Induced X-ray Emission (PIXE) or a microdestructive method such as laser induced plasma (or breakdown) spectroscopy (LIPS or LIBS). In general, for archaeological bronzes LIPS depth profiles can provide more reliable compositional information than XRF and PIXE since the former can analyse the metal bulk up to several hundred microns whereas the corresponding range of the latter is limited to several tens of microns. However, LIPS can only provide indirect information on the presence and condition of the metal substrate beneath the earthy concretions and corrosion stratifications, through the examination of the behaviour of the elemental profiles. Thus, the preliminary selection of the best areas to analyse by means of an effective method providing information on the material strata, as well as on the presence and position of the metal surface beneath the stratification, would be very helpful. Moreover, such a non-invasive microstratigraphic characterisation of archaeological bronzes could also be very useful in order to design suitable conservation–restoration treatments.

Within this framework, here, we explore the potential of THz spectroscopy for collecting the mentioned stratigraphic information before LIPS analysis and any material removal conservation treatment. THz waves allow distinguishing different dielectric layers, which reflect the wave packet (echo signals) according to their corresponding refractive indexes. As each pulse corresponds to each layer, from which depth profiling can be obtained by using the time of flight method. To date, no alternative microtomographic approaches are available for such a challenging characterisation, since optical methods are inapplicable while X-ray or neutron imaging does not offer enough discrimination and resolution, respectively.

Along the last decade, several applications of the THz-time domain spectroscopy (THz-TDS) have been pioneered in various fields by exploiting their potential to distinguish different dielectric layers. In particular, THz TDS has been used as non-destructive tool in biomedical engineering [2], physics [3], astronomy [4], communications [5], genetic engineering [6], pharmaceutical quality control [7], medical imaging [8], defence and security [9], and cultural heritage [10]. In the latter field THz spectroscopy and imaging have been successfully used for characterising paint layers [11–13], parchment and papyrus manuscripts [14,15], whereas only a preliminary work was reported on archaeological bronzes [16].

In this work, THz spectroscopy has been used for characterising a set of laboratory samples. These were suitably prepared in order to measure refractive indexes of some minerals of interest, roughly simulate the mineralisation stratigraphy, and investigate the corresponding reflection behaviours. Hence the THz reflectometry has been applied on a set of authentic archaeological bronze artefacts where complex

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E-mail address: i.cacciari@ifac.cnr.it (I. Cacciari).

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behaviours were observed, depending on surface texture and corrosion phenomenology. LIPS elemental depth profiles were measured in the same spots of the THz TDS analyses in order to investigate possible correlations between the behaviours detected by these two complementary spectroscopic approaches. The discussion of the results achieved allows drawing some general conclusions on the archaeo-metallurgical potential of the THz spectroscopy and on exploitation of the present analytical combination.

2. Materials and methods

2.1. Terahertz time domain spectrometer

A commercial THz Time Domain Spectrometer (TDS) with a bandwidth of 0.1–2.5 THz was used in the present study. The system is equipped with a 1.550 μm ultrashort fibre laser with a pulse duration <80 fs (FemtoFErb 1560 produced by Toptica). A 50/50 splitter divides the laser beam into two channels terminated with LT-GaAs based photoconductive antennas (PCAs): emitter and detector, respectively. The single mode fibre-pigtailed design allows for a flexible arrangement in either transmission or reflection geometry. Both the PCAs are coupled to an elliptical silicon lens and then to a hemispherical TPX lens for collimating/focusing and focusing/collimating the THz beam [17,18].

The emission path includes a fast scanning delay stage. In order to vary the arrival time of the signal with respect to the pulse used for detection, a delay stage is introduced in the generation arm. By scanning the delay line, the phase and the electric field amplitude of the THz waveform can be sampled as a function of time. A LabView® software registers and saves the electric field amplitude from a digital lock-in amplifier that measures the signal from the detector.

Laser, fibre splitter, delay stage, driver electronics, power supply as well as the system control and data acquisition are all housed in one box (60 x 60 x 25 cm). The system is equipped with a USB data interface to allow versatile control via Labview® software.

The present measurements were carried out using the reflection geometry by fixing the incident and collection angles at about 30° to the sample surface normal, the corresponding plane, and focal position. To this goal the PCAs were mounted in a suitable yoke and an aiming laser beam was used in order to control the focus position. This set up allowed to rule out the typical alignment procedure using a metallic mirror and guaranteed a very good reproducibility.

The diameter of the THz beam at the focus position was measured using the knife-edge technique. Once the system has been optimized, a smooth metal edge is inserted in the beam at the test point and it is translated across the beam, gradually obscuring it. The THz signal is recorded at consecutive knife-edge positions. The maximum of the time domain peak may be plotted against the edge position, and for a perfect Gaussian beam the dependence is the well known error function. Once the data have been fitted, the beam waist (i.e. the spot diameter at the focus position) can be calculated.

2.2. Surface roughness

In this work THz reflection TDS has been used to analyse the corrosion layers of a set of bronze archaeological objects. Generally significant amplitude decrease and broadening were observed on the reflection peaks of their outer layers. These phenomena appeared to be strongly dependent on the surface morphology thus a dedicated insight was carried out. Surface textures were measured using a 3D digital microscope [19–21] based on the shape from focus technique. A stack of images of the same scene, are acquired at different focal planes (i.e. heights). All the images are then processed in order to extract all the pixels in focus. These are correlated to the heights at which the images have been taken and a 2D data height map is readily obtained, which allows calculating the surface roughness parameters according to the well-known formulas.

In order to compute the roughness of the sample within the THz spots, evaluation areas of about 2×2 mm were framed with the 3D microscope around the THz spots, which were highlighted by the laser pointer.

2.3. Samples

Multilayer samples have been prepared in order to roughly simulate the actual corrosion stratigraphy in which the metal surface is covered by layers of copper corrosion products. We have firstly considered the case of two superimposed artificial layers placed on a suitable clamp to eliminate possible air gaps: a small slab of copper mineral (such as malachite, tenorite or cuprite) achieved using a press on a copper plate (0.5 mm thick). In a second set of samples we replaced the mentioned copper plate with an archaeological bronze fragment, which presented surface roughness higher than the copper plate. More complex situations have been also simulated including three layers: cuprite and malachite on a copper plate or the archaeological bronze.

2.4. LIPS

The THz microtomographic imaging has been combined with laser induced plasma spectroscopy (LIPS) elemental depth profiling. LIPS can perform depth profile analysis by applying a series of subsequent laser pulses on the same spot area of the object thus providing chemometric information on the outer layers and the bulk of the object under study. This makes LIPS one of the most suitable techniques for probing the distribution of elements in archaeological objects such as bronzes, where traditional sampling would produce unacceptable damages. However, LIPS is a micro-destructive technique (the diameter of the crater ranges between about 120–250 μm for a number of pulses of about 100 and 2000 respectively) and then it would be desirable to perform a limited number of measurements according to a suitable preliminary selection of the measurement site, in order to achieve a representative elemental characterisations of the artefact. In particular, archaeometrical studies of copper alloy artefacts [22], which presented deep corrosion and mineralization phenomena, have highlighted the limitations of "blind" choice of the LIPS measurement sites. Thus for example, the thickness of the corrosion layer in some parts of the object can be relatively large thus preventing LIPS from reaching the metal bulk. In this work we show as the knowledge in advance of the layer structure via THz imaging can allow a careful selection of LIPS measurement sites and provide a stratigraphic characterisation, which can be usefully integrated with the elemental depth profiling.

LIPS measurements were performed using the set-up described in details elsewhere [23]. Shortly, it is equipped with a Q-Switching Nd:YAG (1064 nm) laser, four high resolution Czerny-Turner spectrometers (2.400 grooves/mm) combined with CCD linear array detectors, which cover the spectral range between 200–630 nm with a resolution of about 0.1 nm. The system has been calibrated for the analysis of copper alloy artefacts, also taking into account some depth-dependent phenomena affecting the response of the system in deep depth profile measurements [24].

3. Results and discussion

In Fig. 1 the THz signals reflected from double layers samples (parallel slabs of copper minerals on smooth copper plate and archaeological bronze, respectively) are compared. All of them include two peaks of different amplitudes and shapes. Part of the incoming THz pulse is reflected at the first interface (i.e. air/corrosion material) and is responsible of the first peaks shown in Fig. 1, whose different amplitudes are determined by the different refractive indexes of the minerals. The remaining part of the incoming THz pulse is transmitted through the mineral slab, reflected by the metal surface, transmitted back through the former, and eventually detected by the receiving PCA. The specular