Non-invasive technological study of bronze artefacts of historical and artistic interest using nuclear techniques: Imaging and Neutron Diffraction

Student: Francesco Cantini francesco.cantini@unifi.it

Tutor: Francesco Grazzi (CNR-IFAC) <u>f.grazzi@ifac.cnr.it</u>

Co-Tutor: Lorenzo Giuntini (UNIFI / INFN) giuntini@fi.infn.it

Neutrons weakly interact with atomic nuclei by nuclear scattering or absorption, penetrating deep into the matter. The physical law that regulates nuclear interaction changes greatly between the elements and depends on the crystalline structure, making it possible to determine the atomic species involved and their structural arrangement with considerable sensitivity. These characteristics make neutrons a promising probe to investigate metal artefacts in the field of cultural heritage, allowing to analyse even geometrically complex artwork, in a totally non-invasive way. In fact some elements, like hydrogen, have a strong interaction with neutrons, and it is therefore possible to analyse their presence in light compounds (such as alloy mineralization products) allowing to determine the conservation state of the entire volume of the artefact, a result that it is almost impossible to achieve with other techniques.

In this PhD project we propose to address the problem of diagnostic and conservation of ancient metal artefacts by exploiting the following nuclear techniques:

- *Time of Flight Neutron Diffraction:* it allows to measure selected areas of the samples ranging in size from a few mm to a few cm and to quantitatively determine the concentration of the crystalline phases in the investigated volume. Furthermore, by studying the shape and relative intensity of the diffraction peaks in the metal phases, it is possible to obtain indirectly information on the grain size, on the presence and density of flaw and internal stress and on the cold working methods or on the direction of solidification [1-3].
- Neutron Imaging and Digital Tomography: radiographic imaging techniques generally allow the creation of digital data sets related to the morphology and composition of complex objects. Specifically, radiography consists of measuring the intensity of neutrons that pass through a sample, obtaining information on the density, the relationship between the parts and the internal morphology in a similar way to X-ray Radiography. With neutrons, however, it is also possible to analyse significant thicknesses (of the order of centimetres) of heavy materials such as metals. By combining various radiographs at different orientations, a neutron tomography of the artefacts can be obtained. The possibility of having a reconstruction of the entire volume of the object, makes every constitutive and microstructural detail virtually explorable, and can be an essential tool for investigating the manufacturing methods and determining the conservation state. In the case of hollow bronzes, the metal thickness, the presence of fractures, gaps and defects, and the presence of internal materials such as support structures or melting earth can be investigated. Starting from the projection data, it is also possible to reconstruct by software a 3D model of the entire volume of the object, providing conservators with a highly informative and intuitive tool to use. Thanks to the different attenuations of the artefact components, it is also possible to break down the various parts by digitally segmenting the distinct volumes. Moreover, different metal phases can be quantified by evaluating the grey tones associated with each voxel. [4-8]. A significant example of the results obtainable within this framework is reported in Fig. 1, in which it is possible to observe the neutron tomography sections (fig.1(b)) of the head of the "Standing Buddha" statue (Rijksmuseum), along with the reconstruction and segmentation of the different volumes inside the statue. The experiment was performed at reactor BER-II (HZB (Helmholtz Zentrum Berlin, Wannsee, DE).

Among the Neutron Imaging techniques, *Energy Selective Scan* [9-10], provides a very accurate microstructural characterization. This technique is based on the acquisition of a series of neutron radiography (or tomography) at different wavelengths with a monochromatic beam. The use of a monochromatic beam offers the possibility to change the contrast of the image, for the different phases, taking advantage of the abrupt change in the attenuation coefficients at the so-called Bragg cut-off. In fact, for each crystalline phase, depending on its reticular organization, there is a characteristic λ for which the scattering cross section collapses, favouring transmission. This allows to identify different metallic phases, and to obtain clues about the casting temperature or cold working.

BUDDHA (AK-MAK.193), Rijksmuseum - Asian pavilion

Tomoarafia Neutronica



Fig. 1 *Standing Buddha* (Rijksmuseum). **A** Photographs of the head of the statue. **B** Neutron Tomography: frontal section (YZ), sagittal sections (ZX). **C** Reconstruction and segmentation of the different volumes inside the statue. In yellow: earthy filler (casting core); in green: the portions affected by corrosion at the interface between the bronze and the casting core; in red: corroded external surface of the iron rod [7].

This project also makes use of an important collaboration with The Opificio delle Pietre Dure (OPD) that is one of the great national centres for the restoration of historical-artistic artworks, with decades of experience in diagnostics and in the restoration of bronze metal artefacts. This partnership will allow access to the archive of metal alloy samples of all artefacts that have undergone a restoration at OPD, and will also make it possible to analyse unique works of art, currently under restoration, that would otherwise be inaccessible.

The research activity will also include participation in the CHNET - NICHE project, which involves the development and optimization of a thermal neutron imaging and tomography system at the LENA reactor in Pavia. It will be possible to actively take part in the development of the set-up, in the calibration of the instrument and perform the very first applications to Cultural Heritage artefacts.

This project will play an important role in historical-technological research for ancient bronzes and will contribute, to the development of an analytical protocol for bronze diagnosis combining traditional analytical techniques with the nuclear ones, such as Imaging and Neutron Diffraction that will allow to obtain results impossible to achieve in other ways.

BIBLIOGRAFIA

- [1] F. Grazzi, L. Bartoli, et alii (2010). Characterization of copper alloys of archaeometallurgical interest using neutron diffraction: a systematic calibration study. *Anal. Bioanal. Chem.* 397:2501–2511. doi:10.1007/s00216-010-3815-4
- [2] F. Grazzi, F. Civita, et alii (2011). Ancient and historic steel in Japan, India and Europe, a non-invasive comparative study using thermal neutron diffraction. Anal. Bioanal. Chem. 400:1493–1500. doi:10.1007/s00216-011-4854-1
- [3] F. Grazzi, E. Barzagli, et alii (2016). Determination of the manufacturing methods of Indian swords through neutron diffraction. *Microchemical Journal* 125 (2016) 273–278. http://dx.doi.org/10.1016/j.microc.2015.11.035
- [4] E. Lehmann, E. Deschler-Erb, et alii (2010). Neutron tomography as a valuable tool for the non-destructive analysis of historical bronze sculptures. Archaeometry 52, 2_272–285. doi:10.1111/j.1475-4754.2009.00480.x
- [5] E. Lehmann, P. Vontobel, et alii (2005). Non-invasive studies of objects from cultural heritage. *Nuclear Instruments and Methods in Physics Research A* 542 68–75 doi:10.1016/j.nima.2005.01.013

[6] F. Salvemini, V. Luzin, et alii. (2017) Archaeometric investigations on manufacturing processes in ancient cultures with the neutron imaging station DINGO at ANSTO. *Physics Procedia 88, 116–122 doi:10.1016/j.phpro.2017.06.015*

- [7] Cantini, F. (2017). Caratterizzazione non distruttiva della microstruttura e delle metodologie produttive di manufatti storici in bronzo e acciaio dell'india e del sud est asiatico mediante l'utilizzo di tecniche avanzate di imaging neutronico, LM in Scienze per la Conservazione ed il Restauro, Università degli Studi di Firenze.
- [8] F. Grazzi, F. Cantini, et alii (2018). The investigation of Indian and central Asian swords through neutron methods". Journal of Archaeological Science. https://doi.org/10.1016/j.jasrep.2018.06.010.

[9] L. Josic, E. Lehmann, et alii (2011). Energy selective neutron imaging in solid state materials science. Nuclear Instruments and Methods in Physics Research A 651_166–170 doi:10.1016/j.nima.2010.12.120

[10] F. Salvemini, F. Grazzi, et alii (2012). Quantitative characterization of Japanese ancient swords through energy-resolved neutron imaging. Journal of Analytical Atomic Spectrometry ISSN: 0267-9477