Journal of Instrumentation

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PUBLISHED BY IOP PUBLISHING FOR SISSA MEDIALAB

RECEIVED: *December 24, 2017*
ACCEPTED: *April 9, 2018*
PUBLISHED: *May 11, 2018*

INTERNATIONAL WORKSHOP ON IMAGING II
4–8 SEPTEMBER 2017
VARENNA, ITALY

A neutron diffraction and imaging study of ancient iron tie rods

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https://doi.org/10.1088/1748-0221/13/05/C05009

Abstract: Milan Cathedral is one of the biggest and widest churches ever built among the other coeval architectures. It had a very long and complex construction history, which started in 1386 and lasted more than four centuries. The dominant style is the European gothic but the lombard tradition has strongly influenced the composition. Gothic cathedrals were diffusely built in Europe during the Middle Age, and each region developed its own local interpretation. However, a common feature of the style was the presence of slender pillars and of many elements able to reduce the horizontal thrusts of the vaults, such as spires, buttresesses, flying buttresesses and tie rods. In Milan Cathedral, tie rods have a fundamental role due to the specific characteristics of the structural system and its complex history. In 2012, a broken tie rod was found and it was substituted with a new one. Therefore, a multidisciplinary research on these elements started, aiming at a deeper material characterization and an *in-situ* identification of local defects. Among non-destructive techniques, several neutron analyses were performed on different samples. We will report on neutron diffraction measurements and neutron resonant capture analysis on part of the original broken tie rod. Moreover, neutron imaging was recorded on other iron tie rods (from an external spire). Results will be useful for an independent assessment and validation of models and of new on-site monitoring techniques, since no other conventional non-destructive technique will allow the same characterization.

Keywords: Inspection with neutrons; Instrumentation and methods for time-of-flight (TOF) spectroscopy

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Contents

1 Introduction

Gothic cathedrals were diffusely built in Europe in the period spanning from 1100 AD onwards, and each region had its own architectural characteristics. However, a common feature of the style was that the main weight of the cathedral structure is carried downwards by slender pillars (about 30 m high in Milan Cathedral) along the nave and the side aisles.

Despite the ribbed vaults typical of gothic architecture have a lower horizontal thrust than barrel vaults, the high weight and structure slenderness determine not negligible lateral forces which must be properly balanced through adequate structural elements. In many buildings an external system of flying arches and buttressing was developed, thus applying counter-acting force sideways towards the walls. In other buildings an alternative solution was used, incorporating reinforcement in the form of iron tie rods (Heyman, 1995).

Milan Cathedral is nowadays one of the biggest and widest examples of gothic architecture in the world, and it had a very long and complex construction history, started in 1386 AD.

Its dimensions are impressive: the main nave tie rods are 18 m long, while lateral ones reach "only" 9 m (Ferrari da Passano, 1988). Consequently tie rods have massive dimensions. The manufacturing of such long and heavy elements must have been not the lesser problem for the architects of 15th century, when the iron technology was in the transition stage from the bloomer (low-temperature iron reduction) to the blast (high-temperature) furnaces.

In 2012, a broken tie rod was found and it was substituted with a new one (M. Vasic, 2015). Therefore a multidisciplinary research on these elements started.

The actual stress of tie rods placed inside the Cathedral was estimated (M. Vasic, 2015) by using the dynamic procedure described in (Tullini and Laudiero, 2008). Limit analysis was employed with the aim of understanding the structural behavior of the vaults and finding load paths inside the

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masonry (Vasic and Coronelli, 2014). In order to provide a deeper material characterization, both a metallographic investigation (Bellanova et al., 2015) and a toughness test (Gianneo et al., 2017) were carried out on the original material. Finally several studies were performed to define non-destructive techniques able to detect dominant flaws. An *in-situ* validation of them was performed as well.

However many questions remain unsolved on the subject: how the bars were manufactured? Where were they produced and where did the iron come from? How is their conservation status? The tie rods have been obviously realized in many parts and eventually assembled; however, the degradation of the surface after some centuries and the operative difficulties in investigating a sample suspended at 30 m height made it difficult to study the rods while in operation. Iron bars were placed *in-situ* around 1400 AD and possibly they were not substituted during the centuries. Therefore, a deep characterization of this metallic reinforcement would be greatly relevant for the study of both a significant sample of medieval technology and a structural element that remained in full operation for more than 600 years.

1.1 Background and previous results

Following a classic metallurgical approach, some preliminary results were obtained (Bellanova et al., 2015). The material is extremely heterogeneous both in terms of microstructures and defects. Ferrite and pearlite are the prevalent microstructural compounds, though some cementite was also recognized. Their distribution over the cross-section is extremely variable and oscillates from 0 to 100%. In general a mainly ferritic structure was identified. Different types of flaws such as micro-cracks, micro-porosities, voids, slag inclusions were identified. Dendritic slag inclusions of silicate, probably produced during cooling, characterize ferritic microstructure. Also spheroidal graphitic carbon was identified over the section where ferritic structure is prevalent. Fine pearlite seems to grow around carbon nodules. These kinds of slag are completely absent in pearlitic structure, where discontinuities consist in microcracks, voids and porosities. Usually, inside the crack iron oxides inclusions were recognized. A good agreement between hardness tests results and microstructural findings was shown. The material heterogeneity was confirmed by the hardness variability which ranges from 50 HRC and 79 HRC. Distinctive hardness values related to pearlitic, ferritic and ferritic-pearlitic structure were estimated. They correspond respectively to 76HRC, 65HRC and 54HRC. Inverse analysis was performed on the Rockwell indentation curves. The results show a good agreement with the metallographic observations. A higher strength corresponds to a higher percentage of pearlite while the mainly ferritic microstructure exhibits a more ductile behaviour. Nevertheless, some estimated values are unreasonable possibly due to some drawbacks which affect the implementation of the adopted model on ancient metals.

The remaining tie rods were inspected *in-situ*, using a classic hammer test in order to identify the active elements, compute the main dynamic characteristics (natural frequency, mode shapes and damping ratio) and estimate the actual state of stress (M. Vasic, 2015). The natural frequencies of vibration, and hence the actual stress which should in principle be equal in each nave, were found to be different. This emphasizes the relevant effects of the load changes during the centuries in the historical buildings. The axial force is ranging from 0 to 643 kN. In the tie rods with a level force higher than 80 kN, almost a linear trend between the natural vibration frequency and the estimated load can be observed. For lower level of axial force, the boundary conditions effects are more significant, and the structural element behaves as beam. Taking into account the mechanical properties of wrought iron, the computed actual stresses are ranging from 0 to 140 MPa. The recorded response was analyzed by computing the Frequency Response Function and by using the Frequency Domain Decomposition (Guidobaldi et al., 2014). Both tools confirmed the presence of splitting of the first modal peak in four tie rods. In the literature this phenomenon is often associated to the presence of damage (non-visible cracks).

Toughness tests (Gianneo et al., 2017) confirmed the presence of inclusions which affected the crack propagation. Nevertheless, the computed critical stress intensity factors show a good repeatability oscillating from 41 to 45.3 MPa $m^{1/2}$. An unexpected result was given by stress intensity factor threshold value (for fatigue crack growth) which is high also for a modern steel (about 5.6 MPa $m^{1/2}$).

As concerns the *in-situ* flaws detection by using non-destructive techniques, the effectiveness of other established methods in Mechanical Engineering is being tested (Bellanova, 2017). In order to provide further characterization mainly for the inner part of the iron bar (where the estimated data are most questionable) we carried out a neutron-based study, also to prove previous proposed models and investigations.

In this scenario, neutrons are the most suitable technique: they were indeed more and more used in archaeometallurgy (the branch of archaeology studying ancient metallic samples) (Grazzi et al., 2011; Kardjilov et al., 2006; Kardjilov and Festa, 2017; Di Martino et al., 2017). The choice to perform neutron-based analyses derives from a three-fold motivation: 1) the sample is an ancient artefact, and non-destructive analyses should be used to preserve its uniqueness; 2) no cleaning should be performed on the sample — we thus want to study both the corrosion layers or deposits and the inner parts; 3) the sample is a bulky sample, and we want to infer the mean bulk composition, not only the surface composition.

2 Materials and methods

2.1 Samples

The main sample comes from a part of the original broken tie rod of Milan Cathedral. It has a rectangular cross-section. Its surface is very rough and is characterized by a layer, with thickness of 0.2–0.3 mm, which could be calamine (an oxide produced during the hot working) coupled with a coherent dust layer built-up in the ages. A picture of the sample is shown in figure 1. Sample sizes are about $85 \times 55 \times 840\ \mathrm{mm}^3$, and 30 kg mass.

Further samples comprise a wedge, used as “closing” of the iron tie rod to the pillar, and two smaller iron tie rods, coming from the outside of the building: they were used to reinforce a spire, and have a degraded surface, mainly due to atmospheric exposure. They have a circular section of about 2 cm in diameter (see the following section on results).

2.2 Neutron investigations

Time-Of-Flight (TOF-) neutron diffraction (ND) was carried out at the pulsed spallation neutron source ISIS (UK), using two different beamlines: INES (Imberti et al, 2008) and ENGIN-X (Dann et al., 2004). The INES station is often devoted to archaeometric analyses, and is thus equipped

Figure 1. Portion of an ancient tie rod from Milan Cathedral (1400 AD).

with a specially developed frame conceived for handling big and delicate samples. In our case, we had to use a dedicated sample holder, able to hold up very heavy specimens of 30 kg. We choose a screw-jack, designed and realized by the ISIS internal laboratory.

INES offers the unique possibility of performing simultaneous ND and Neutron Resonant Capture Analysis (NRCA) measurements, and, through a simplified radiography apparatus, to check for the existence of interesting features (cracks, heterogeneities) in the depth of the sample (thus guiding the selection of interesting regions to explore). A system of "jaws" (i.e. beam limiters) can be used to shape and reduce the neutron beam size and to select the gauge volume of interest in the sample even in the millimetric range. The measurements were conducted in air, and the alignment was made through a laser pointer. NRCA spectra were recorded detecting resonance peaks occurring in cross sections of neutron-induced capture reactions, as a function of neutron energy. These peaks can be used to identify elements in materials. Details on the NRCA technique can be found for instance in the literature (Kardjilov and Festa, 2017). Here, we just mention that in NRCA energies of adsorbed neutrons are identified through the TOF technique; this means that the NRCA detector (in this case a YAP scintillator) records the arrival time of neutrons into the sample. The resulting spectra are thus shown as a function of time. We analyzed a full series of spots on the tie rod, in order to have a deeper insight of the sample. The choice of such spots has been guided by preliminary radiographs performed on site, as explained above.

Further TOF-ND was carried out at ENGIN-X, a station especially designed for strain measurements. In this case, we had at our disposal also an unstressed reference sample.

The ND data were processed using the Mantid software (Arnold et al., 2014), for data normalization and correction, and then were analysed with the Rietveld refinement techniques using the GSAS (General Structure Analysis System) code (Larson and Von Dreele, 2004) with the EXPGUI interface (Toby, 2001).

Finally, thermal neutron radiography (NR) experiments have been performed on the RAD imaging station of the BNC, H (Kis et al., 2015). The imaging setup had a circular Field-of-View (FoV) with a diameter of 180 mm, and a spatial resolution of 0.24 mm. The rods were not cleaned before experiments. The FIJI code was used for a later image processing to produce the so called attenuation images. Images are flat-field and dark current corrected.

3 Results and discussion

3.1 Neutron results

Several neutron investigations were carried out on tie rods from Milan Cathedral. Each technique was mainly devoted to a particular aspect in the characterization of the samples. In particular, by

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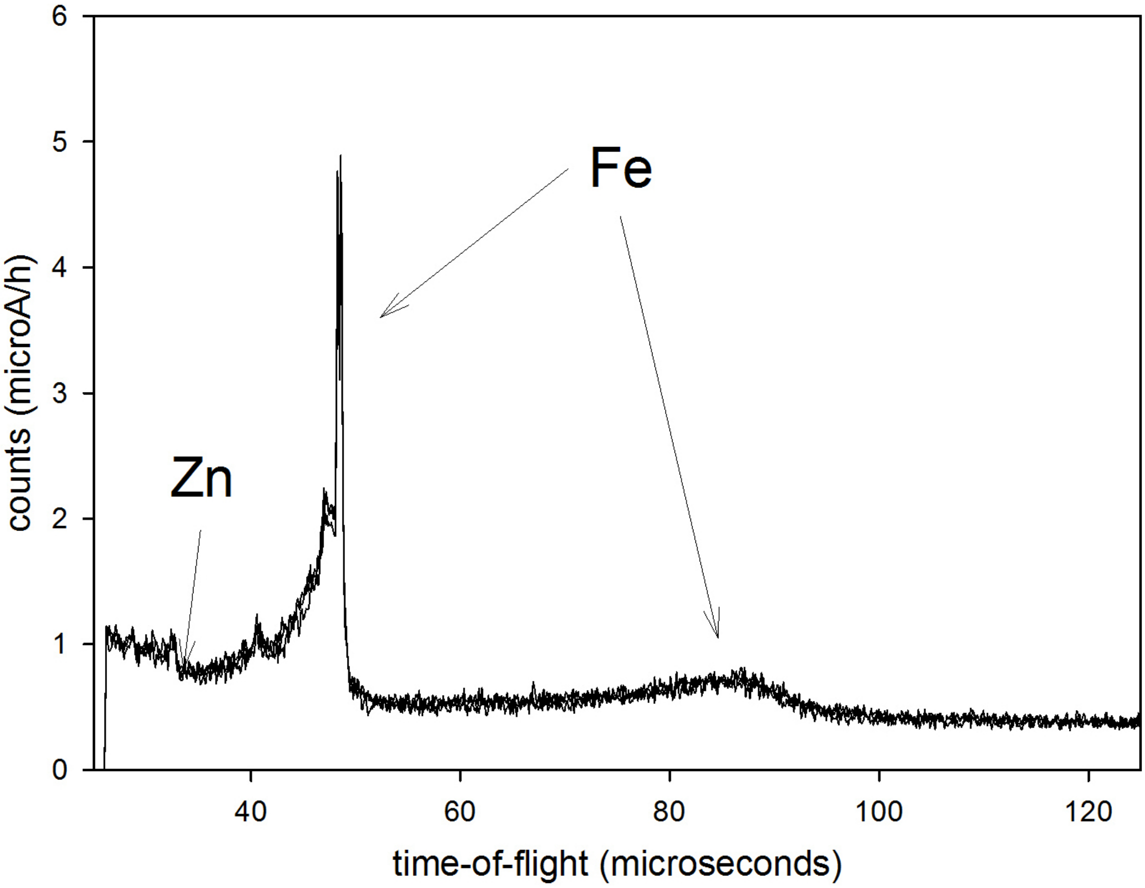

Figure 2. NRCA results on iron tie rod. Three different points along a horizontal direction were measured.

NRCA we could derive elemental composition, while TOF-ND describes the crystalline structure of the material, thus giving indication on the mineralogical phase composition, but also (in a dedicated configuration) on the inner stresses. Finally, neutron imaging displays the inner morphology of the samples through neutron attenuation coefficients.

3.1.1 ND and NRCA results

The original tie rod was analysed by TOF-ND in several spots, along the vertical and horizontal directions of the sample. Despite the neutron beam was not crossing all the inner surface, we estimated, by a preliminary radiography, that at least 2 cm of iron were crossed. All neutron diffractograms revealed only ferrite peaks. No signal from corrosion phases or phases containing carbon was detected. We could thus infer that the outer surface (about 2 cm in thickness) was in a good conservation status, since no iron oxides or hydroxide were revealed. By NRCA the presence of iron was confirmed. However, a very small peak could be assigned to Zinc, with no other relevant element. The NRCA spectrum is displayed in figure 2. In the present investigation it was not possible to derive a quantitative concentration, thus the results are only qualitative. Yet, zinc element should be a minor component and it could be spatially related to outer region of the samples. One hypothesis could be the zinc was a contaminant, but another could be to associate zinc to the presence of the calamine mineral (chemical formula: $Zn_4Si_2O_7(OH)_2 \cdot H_2O$).

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Starting from ND data, recorded at ENGIN-X, an attempt of studying the residual stress in the inner part of the broken iron tie rod was carried out. We indeed derived preliminary and a clear map of strains along one section of the sample is displayed in figure 3.

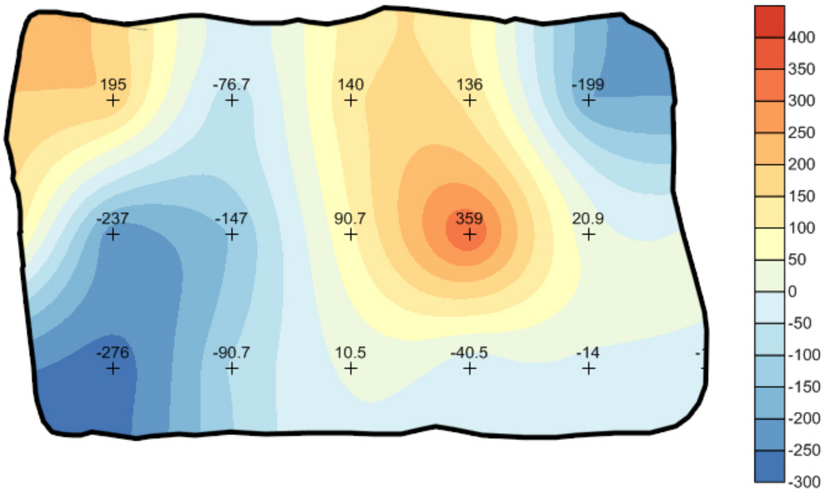

Figure 3. Map of the strains derived by ND analysis at ENGIN-X. A non homogeneous distribution of strains is clearly visible.

3.1.2 Neutron imaging results

Concerning radiography, a first trial made at INES (during the alignment procedures), revealed only the edges of the tie rod in transmission: the section of 8×8 cm was practically opaque for neutrons. This is consistent with the mean free path of neutrons within iron materials (about 2 cm). In fact, we successfully recorded neutron imaging on the smaller samples (diameter of 2 cm), as displayed in figure 4. The experiments were carried out at RAD beamline (BNC, Hungary). In figure 4 the visible appearance and the radiograph of a tie rod is shown. NR returns information of the transmitted beam, hence revealing regions with different neutron attenuation coefficients. In the following NR images, brighter parts are related to high attenuation coefficients (i.e. elements with higher neutron cross sections), and darker parts are due to low attenuation coefficients (i.e. voids, or elements with low neutron cross sections). We highlights that usually hydrogen-bearing compounds are clearly visible in NR, since hydrogen has a very high attenuation coefficient.

The inner part seems quite homogeneous. Some bright regions are visible, mainly due to the increased thickness (for the superposition of different parts of the tie rod). However, a very bright layer is visible also on the surface of the tie rod. See for example, in figure 4, some points marked by a red asterisk. In this case, to explain a very high attenuation, one could infer that elements with high neutron attenuation coefficients are present, for example hydrogen. So, the surface layer could be affected by an alteration patina, containing hydrogen, i.e. similar to FeOOH (commonly known as rust). Besides, also some H-bearing pigments could be considered too, since some painting remains are visible on the surface. On the other side, some voids are visible too. For example the point marked by a blue asterisk denotes a sort of inner “empty line” within the tie rod.

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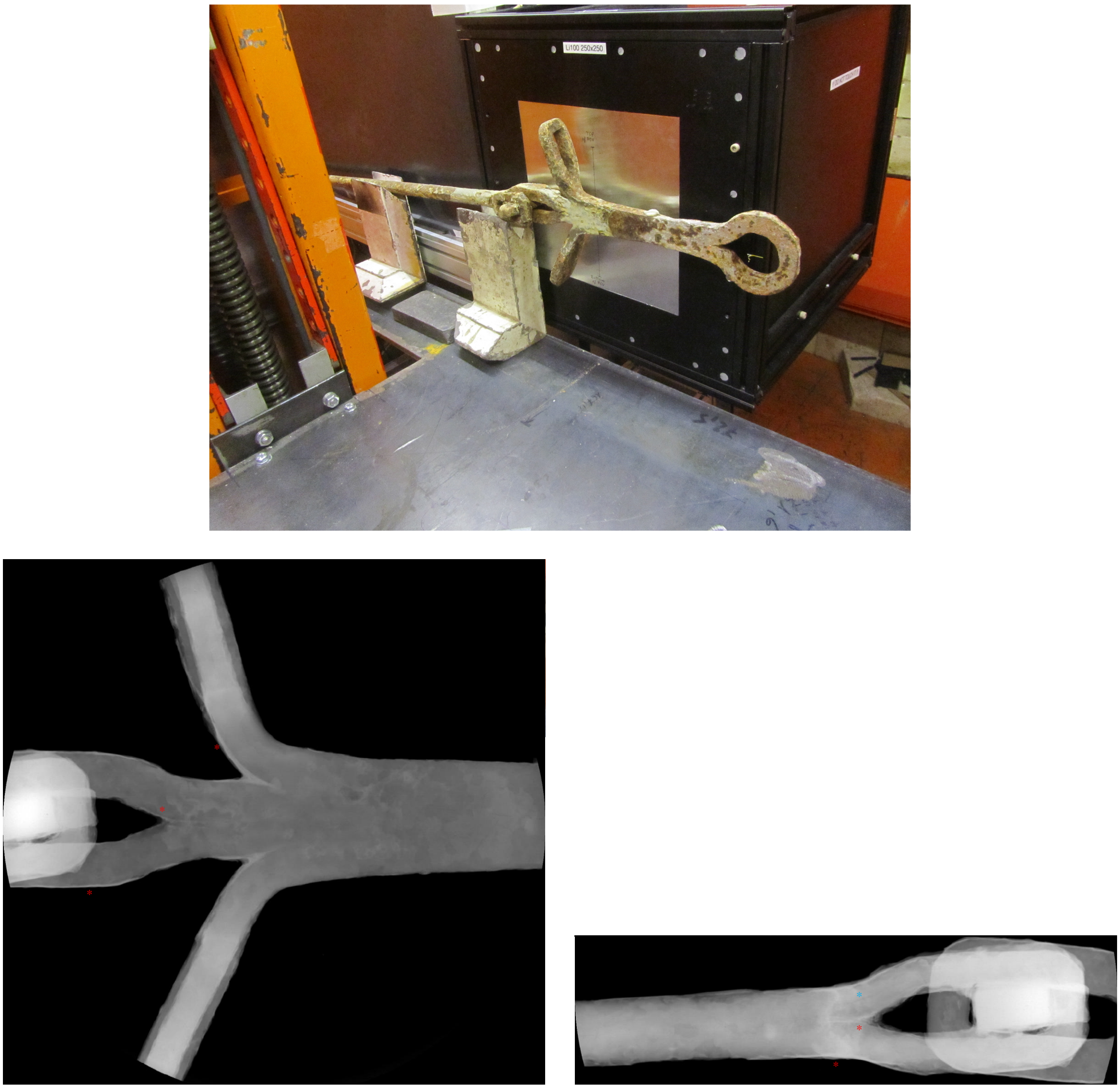

Figure 4. Visible appearance and neutron radiograph of a tie rod from an external spire of the Duomo Cathedral. See text for details.

Figure 5 reports another radiograph from a different tie rod. In this case the effects of atmospheric exposure are already evident from the picture. Again, points marked by a red asterisk identify some patinas or pigments (containing hydrogen), while blue asterisks denote voids. The biggest void is clearly visible by naked eye. This could be a point where the alteration process begun (being an access for water or humidity to penetrate the rod). Another "empty line" is clearly highlighted by neutron imaging (visible also in figure 4). In both cases, due to their position and behaviour (following the "ring" shape of the tie rod), these "empty lines" could be associated with the manufacturing technique too.

We stress that many of these defects are not visible by naked eyes, and that no other non-destructive technique could return similar results and infer the inner morphology of the tie rods

These results will be thus useful for an independent assessment and validation of models and of new on-site monitoring techniques.

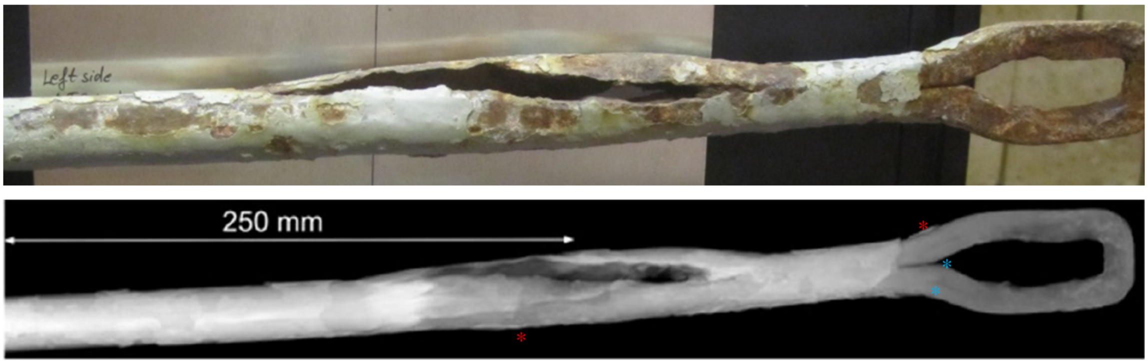

Figure 5. Visible appearance and neutron radiograph of another tie rod coming from an external spire. Crackings due to the atmospheric exposure are evident, but also other interesting inner details. See text for further comments.

4 Conclusion and future perspectives

From our non-destructive neutron based study on ancient iron tie rods we could derive the presence of ferrite phase. By NRCA, single elements could be detected, and we inferred the presence of iron, as a main component, and of zinc, as impurity. The absence of corrosive phases in the outer part of the material indicate a good conservation status of the material itself. However, strain information was also obtained, displaying a non homogenous distribution. Finally, by NR we could return many details on the inner morphology and derive some hints on the manufacturing process. In fact, the behaviour of cracks and voids, clearly following the curvature in the final part of the specimens, suggest that at least two parts of iron were assembled to fabricate the 2 cm iron tie rod.

Our neutron study derived very useful information, without preparation, or sampling and in a non-invasive way. Thus, neutron techniques could be always applied to archaeometallurgical samples prior to other investigations.

We stress that no other conventional non-destructive technique will allow the same characterization, for the benefit of the cultural heritage research on archaeometallurgy and this study could be really important to test new on site monitoring techniques.

Neutron based techniques are in continuous evolution and future challenges (some already available) include: (i) the use of combined X-ray and neutron measurements, thus acquiring complementary information, (ii) higher resolution detectors (both for sensitivity and spatial resolutions), and (iii) energy resolved measurements, allowing for instance the mapping of single phases/elements within artefacts (Lehmann, 2017, Salvemini, 2017, Vitucci, 2018).

Acknowledgments

The CNR-STFC agreement 2014–2020 (No. 3420 2014–2020) concerning collaboration in scientific research at the ISIS Spallation Neutron Source is gratefully acknowledged. RAD access at BNC (H) was possible thanks to IPERION CH Grant Agreement n. 654028 (in the framework of Horizon 2020). We warmly thank Giulia Benati for her kind assistance and Francesco Aquilano for very valuable discussions.

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