



TECHNICAL ARTICLE

Characterization and Technological Origin Identification of Ancient Iron Nails

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Metallurgical analyses and mechanical tests were performed on two ancient iron nails (dated to the seventeenth and eighteenth centuries) found at a private estate in the village of Limone sul Garda, which is located on Lake Garda in the northern Italian region of Lombardy. The nails were characterized via various metallurgical methods to assess their matrix composition, microstructure, and nonmetallic inclusion type, morphology, and distribution. These investigations elucidated the manufacturing process of the nails. The results indicated that the nails were produced by different forging techniques, and it was hypothesized that the steel utilized was obtained via two different methods (direct and indirect ore reduction), which were still in use at that time.

INTRODUCTION

Unusual constructions of various dimensions stud the Brescian shore of Lake Garda—the largest lake in Italy—and attract the curiosity of visitors. These structures are ancient lemon gardens (Fig. S-1 [1] in the online supplementary material) called “lemon houses.” Some of them have been recently restored, e.g., the *Castèl* and *Tesòl* lemon houses, whereas others will be restored in the future. The history of these constructions dates back many centuries. Citrus fruits, such as lemons, oranges, cedars, and citrons, came to the Lake Garda during the thirteenth century, brought by the monks of the San Francesco Monastery of Gargnano.^{1,2} Later, citrus fruit trees spread from their garden in Gargnano to other towns along the lake. In the sixteenth century, Bongianni Grattarolo wrote: “For nearly ten miles along the lake, from Salò to Gargnano, there are many gardens whose amenities do not pale in comparison with what the poets wrote of Atlantis, Alcino, and the Hesperides, full in every season the year of all those fruits with the golden peel”.³ The cultivation of citrus fruits thrived in the early seventeenth century in Limone sul Garda. In the second half of the seventeenth century, the existing lemon gardens were expanded, and new ones were built. In those years, the sale of lemons increased, and the poor economy of the region was revitalized.

A map of the *Reamòl* lemon house (1724–1725) in Limone sul Garda drawn by Giovanni Battista Nolli is shown in supplementary Fig. S-2. The lemon houses of Limone sul Garda were described by J. Wolfgang Goethe in his *Italian Journey* as follows: “(September 13, 1786)... We sailed past Limone, with its terraced gardens perched on the hill slopes: it was a spectacle of abundance and grace. The entire garden is composed of rows of square white pillars topped by heavy beams to cover the trees that grow during winter. The slow crossing made it possible to better observe and contemplate this pleasing spectacle”.⁴ Between the end of the nineteenth century and the beginning of the twentieth century, citrus production in Limone sul Garda slid into gradual decline because of competition from other regions, the discovery of synthetic citric acid, and the high maintenance costs of the lemon houses, which were therefore progressively abandoned.

Due to the steep slope of the land, a lemon house was usually built on several terraces connected to each other by stone stairs, as shown in supplementary Figs. S-1 and S-3. A high wall enclosed the grove on three sides to protect the trees from the cold northeastern winds and to guarantee eastern and southeastern exposure. The roof was supported by large pillars connected to each other or to the walls by large chestnut rafters. Small wooden

rafters were nailed perpendicular to the chestnut rafters. The grove was closed in November and transformed into a greenhouse during the winter to protect the trees from the cold. Wide fir planks were nailed to the roof, and wooden planks, glass windows, and doors were installed on the facade. Several nails were used to complete this procedure.

The lemon houses are vestiges of a laborious and productive past and are a heritage to save. Several projects have been launched to preserve or restore them. Owing to the increasing tourist interest in these structures, some lemon houses have been opened daily for visits, and a museum itinerary through some of them has been created¹ with the aim of publicizing the historical and cultural significance of these beautiful structures.

The study of these structures and their parts is also essential for ensuring the accurate restoration of the buildings. Any project involving restoration of ancient building requires the correct raw materials and production techniques⁵ to provide the greatest authenticity. The production process is a part of the heritage, in addition to the products obtained. This is also true for the manufacture of a replica (for example, doors, floors, and gates). The nails used in the lemon houses are no exception. Nails similar to the original ones should be used: they should be made with a similar material and should be hand-made or produced via processes in use 300–400 years ago.

In studies on iron archaeological artifacts, invasive methods based on the analysis of their cross-sections, such as optical microscopy, scanning electron microscopy (SEM), and hardness and tensile tests,^{6–9} were usually adopted. Recently, new techniques have been proposed, including nondestructive experiments.¹⁰ In the present study, two ancient iron nails found in a private estate in Limone sul Garda and dating back to the 1600s and 1700s were examined using various techniques to increase the current knowledge about these artifacts.

MATERIALS AND METHODS

The two ancient nails investigated in the present study are from a private estate in Limone sul Garda. The first nail was found in a lemon-house structure that dates back to approximately the seventeenth century and the second nail was part of an eighteenth century main door. The origin of the nails can be traced back with very high reliability to local production, as Limone sul Garda is well known for the production of iron artifacts in the past, particularly nails. Figure 1 (upper row) shows these finds and their preservation state. The nails had a heavily corroded surface, an irregular shape of the head, and a square section of the shank. It is not possible to report the accurate dimensions of the nails, as their use caused various bends. Because the nails were manufactured via hot plastic

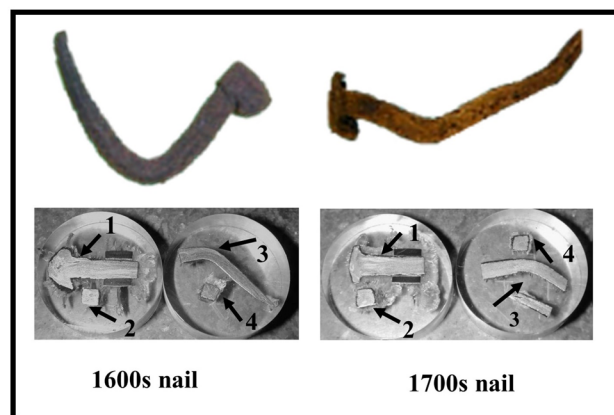


Fig. 1. Examined nails: the nail from the 1600s (left) and the nail from the 1700s (right). Upper row shows their preservation state, and lower row shows cross-sections: 1 head longitudinal section that includes the first shank segment; 2 shank transverse section; 3 longitudinal section of the final shank segment; 4 shank transverse section, close to the bend.

deformation, a certain anisotropy level in the steel microstructure is to be expected. Thus, various samples were taken from longitudinal and transverse sections to investigate the microstructural constitution of the nails, particularly from the head and the shank (Fig. 1, lower row). Cutting of the nails, as well as analysis via destructive tests, was possible because the artifacts were granted to the University of Brescia intentionally for this research. Although archeologists and museum curators may oppose destructive analysis, it is one of the few methods whereby the microstructure of an ancient and corroded steel product can be examined. The chemical composition of the nails was determined via quantometer analysis, using one sample from each nail. Then, the specimens were prepared for metallographic investigation according to standard metallographic grinding and polishing procedures, i.e., grinding with silicon carbide papers followed by polishing with polycrystalline diamond (3 μm and 1 μm). A preliminary examination of the as-polished sample surfaces was performed to obtain information regarding the distribution of nonmetallic inclusions. Subsequently, the samples were etched using a 3% Nital solution (3 vol.% nitric acid in ethanol), which allowed observations of the steel microstructure. The microstructure was examined using both a Leica DMI 5000 M optical microscope equipped with a LAS image analyzer and a LEO EVO-40 XVP scanning electron microscope, in both the secondary electron and backscattered electron detector modes. Semiquantitative chemical analyses of the entrapped nonmetallic inclusions were performed using an energy-dispersive x-ray spectroscopy (EDS) probe, which was coupled with the scanning electron microscope. Vickers microhardness measurements were performed using a Shimadzu Microhardness Tester Type-M under a 500-g load applied for 15 s on the etched longitudinal section to

investigate the correlation between the microstructure and the mechanical properties. Finally, micro-fluorescence (μ XRF) and micro-diffraction (μ XRD) analyses were performed to identify the crystalline phases and to obtain details regarding the chemical composition.

RESULTS AND DISCUSSION

Quantometer Analysis

The results of the quantometer analysis (Table I) indicate that the nails were made of mild steel, with a C concentration of approximately 0.1 wt.% for the nail from the 1700s and a lower C concentration for the nail from the 1600s. The nail from the 1700s also had higher Si and Mn contents. Additionally, differences were observed in the other chemical elements, which can be considered as impurities in the starting ores or in the materials used in the process technology.

Optical Microscopy

To investigate the steel quality, an accurate metallographic examination was performed on the samples shown in Fig. 1. Observations of the nail longitudinal and transverse sections (Fig. 2) with an optical microscope revealed the presence of many large nonmetallic inclusions. In particular, the nonmetallic particles observed in the longitudinal sections of both nails were highly oriented along the forging directions. Analysis of the transverse cross-sections indicated the presence of a large inclusion area fraction, but there was no evidence of a well-defined spatial distribution. The most significant difference between the two nails was the thickness of the surface oxide layer. This layer was thinner in the nail from the 1600s than in the nail from the 1700s, and, for both nails, the oxide layer strongly compromised the matrix by penetrating it. The nail from the 1700s exhibited a smaller amount of inner oxide, with thinner inclusions.

After the morphological analysis of the nonmetallic inclusions, the samples were etched with Nital to evaluate the microstructural constituents and the grain size. Because the nails were manufactured via hot plastic deformation, the microstructural analysis was performed in the longitudinal section of the nails, which was considered to be the most representative section from a metallurgical viewpoint. A collage of several micrographs with $50\times$ magnification is shown in Fig. 3. Both nails had a prevalent ferritic microstructure (with traces of pearlite in the

1700s nail) characterized by a non-uniform grain size, as shown in Fig. 4. Differences in the orientation and elongation of the microstructure were evident in the areas where the shape of the nails changed, e.g., the fillet radius between the head and shank (Figs. 3 and 4). This feature was particularly pronounced in the 1700s nail. Additionally, the surface grains were smaller than those in the inner area, despite the wide range of grain sizes on the surfaces of the nails. These observations can be explained as follows. When equiaxed ferritic grains are plastically deformed, dislocations are generated, and the grains as well as nonmetallic inclusions become elongated and flattened in the direction of working. When this deformation occurs below the recrystallization temperature, the steel becomes stronger and less ductile owing to the strain-hardening mechanism. When additional shaping is required, the steel must first be annealed to restore its ductility via recrystallization and grain growth. During annealing, former strained grains are replaced by non-deformed equiaxed grains that can later increase in size. Therefore, the variable sizes and considerable directionality of the grains in some zones of the nails were caused by partial recrystallization during their production. The thermomechanical processes of hammering and annealing cycles were commonly used in antiquity during the manufacture of metal artifacts.¹¹

Finally, using the micrographs of the etched nails, the flow lines on the longitudinal section were examined. In Fig. 4, according to the flow direction, the flow lines are indicated by various colors. In the longitudinal sections of the shanks, the flow lines are plotted in red, revealing that the flow had only one direction and followed the nail geometry. In the longitudinal sections of the heads, the flow lines had two main directions: the red ones followed the working direction, and the green ones followed the deformation induced during head forging. The flow lines indicate that, in the 1600 s nail, the head was probably obtained via shank bending, whereas, in the 1700 s nail, it was probably obtained through compression stresses applied to the shank by a mallet or a hammer.

According to the nonmetallic-inclusion morphology, microstructure, and flow lines, one difference between the two nails may be the production process. In fact, the 1600s nail exhibited numerous welding lines containing oxide particles that proceeded throughout the nail, which indicates the probable welding/hammering of direct-reduced Fe

Table I. Chemical composition (wt.%) of the nail metal matrices

Nail	C	Mn	Si	P	S	Cu	Al	Ca	W	Pb	Fe
1600	0.038	0.007	0.008	0.0104	0.011	0.074	0.006	0.0112	0.0068	0.0009	99.65
1700	0.107	0.098	0.143	0.0533	0.022	0.010	0.022	0.0384	0.0055	0.0000	99.44

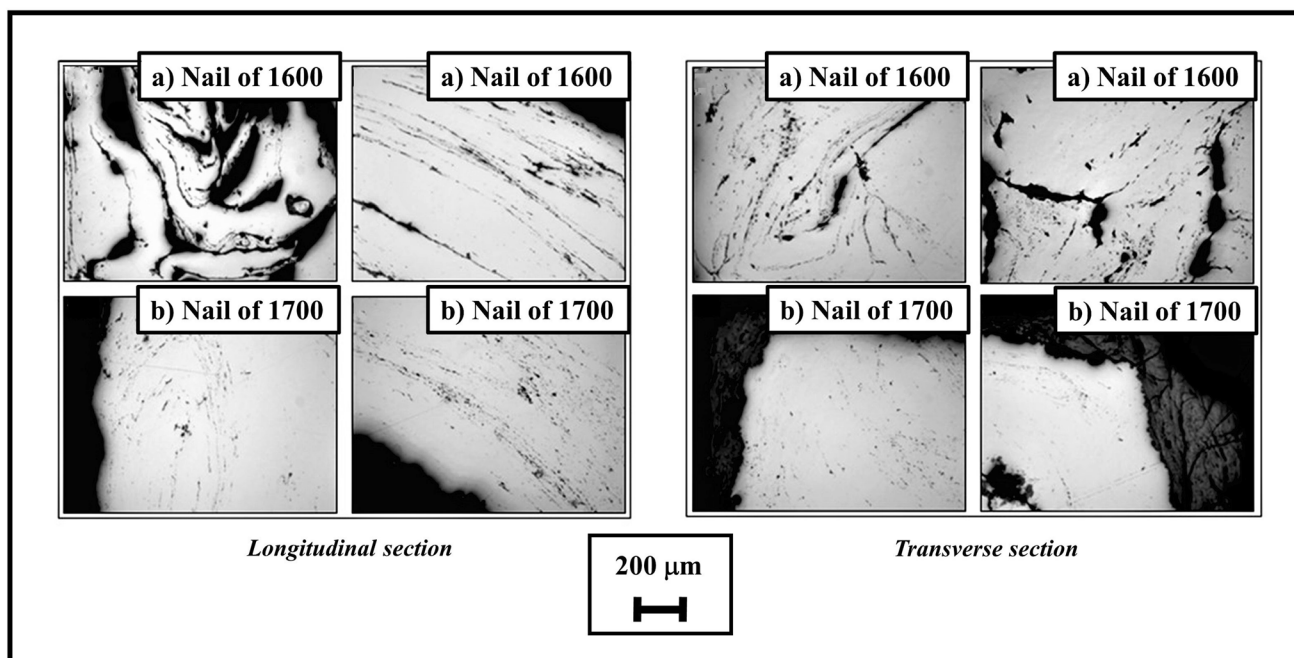


Fig. 2. Micrographs of longitudinal and transverse sections: (a) nail head and (b) nail shank.

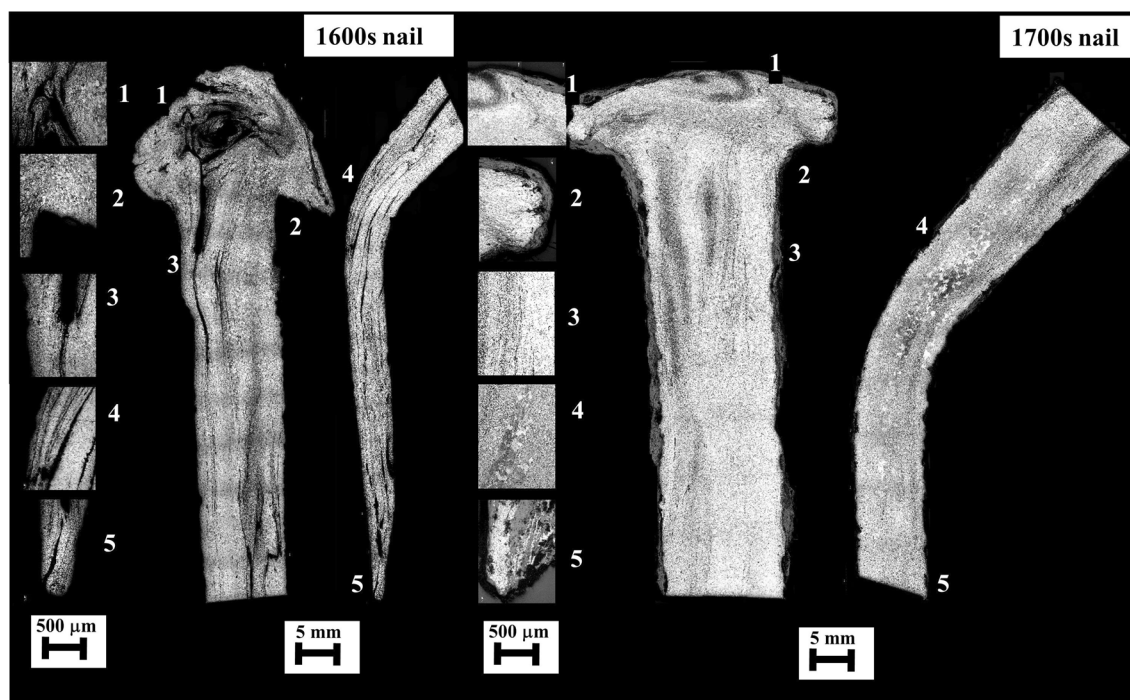


Fig. 3. Macrostructure of the longitudinal section for the 1600s nail (left) and 1700s nail (right). Collage of several micrographs (× 50).

nuggets or bars. In the 1700s nail, there was no evidence of these accentuated welding lines, and the nail appeared to be manufactured from a single rod. The presence of a coarser grain in the shank center may be due to the different forging reduction ratios between the surface and the bulk,

confirming the aforementioned hypothesis. Increasing the thickness of the rod is more difficult to obtain a uniform microstructure in terms of grain dimension through the forging process. The microstructural analyses confirmed the quantometer results.

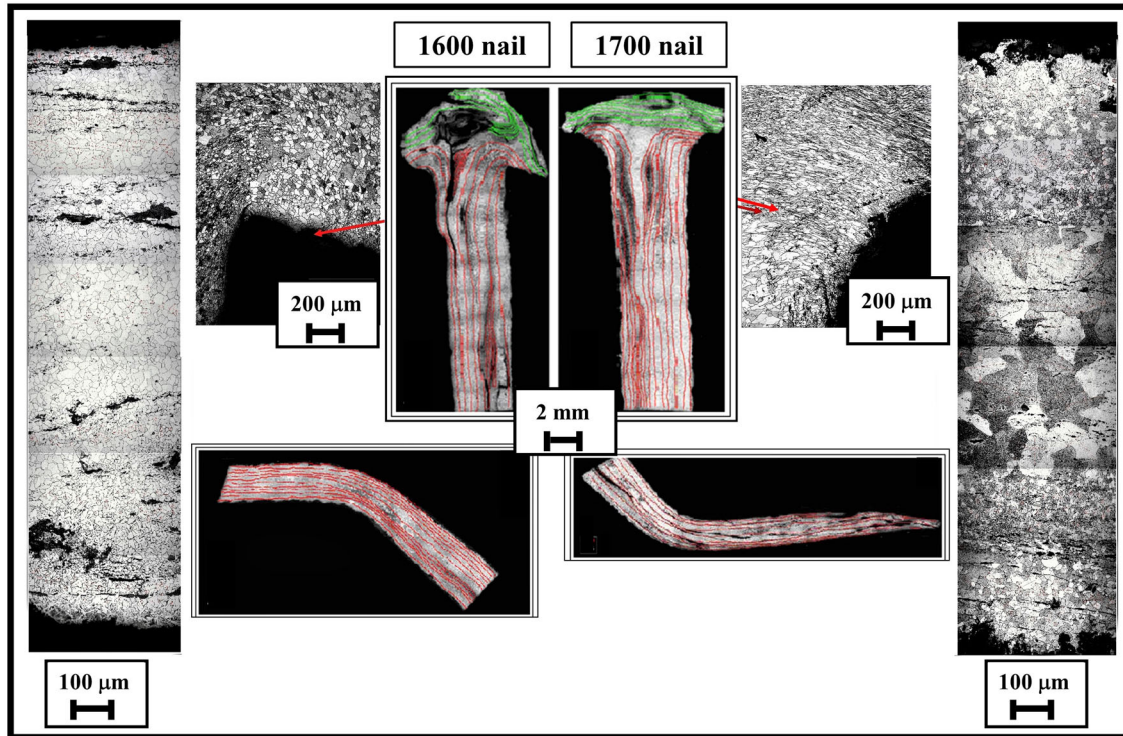


Fig. 4. Profiles, flow lines, and fillet radius of the longitudinal section for the 1600s nail (left) and 1700s nail (right).

Correlation Between Microhardness and Ferritic Grain Size

The average ferritic grain size was measured via a direct method in different nail areas to prevent the numerous oxides present in the nails from affecting the analysis results. Several micrographs collected at a magnification of $160\times$ were examined, and at least 30 measurements were performed for each area. After these measurements, Vickers microhardness tests (HV) were performed on the longitudinal section of both nail shank and head in all zones with changes in the grain size, in addition to the zones characterized by extensive plastic deformation. These values were correlated with the respective ferrite grain size to determine the relationship between the microstructure and the microhardness. Figure 5 shows another difference between the two nails: the microhardness of the 1600s nail was inversely proportional to the grain size, whereas there was no correlation for the 1700s nail. The microhardness values varied in the range of 100–158 HV for the 1600s nail, in accordance with the typical microhardness values of the ferritic phase. In contrast, for the 1700s nail, the microhardness values varied in the range of 122–232 HV. The highest hardness values for the 1700s nail were observed in the head and were probably due to concurrent hardening contributions, e.g., the presence of pearlite traces, small oxide inclusions in the steel matrix, a solid solution effect due to the higher P content, or the drastic plastic deformation in this zone (see Fig. 4). In the first productions via the

indirect method, the process was still to be optimized and such variations in the rods were frequent, especially when the dimension of the piece increases. Thus, the different forging reduction ratios between the surface and the bulk considerably influence the grain dimension and affect the Hall–Petch relationship. Indeed, the strength of a metal alloy increases with a decrease in grain size according to the Hall–Petch relationship. However, heterogeneous microstructures deviate from this relationship depending on the distribution of grain sizes.¹²

SEM/EDS, μ XRD, and μ XRF Measurements of Nail Matrix and Surface Oxides

SEM/EDS Analysis

A chemical analysis of the matrix was performed via SEM/EDS for the as-samples to validate the quantometer measurements. The results confirmed that both nails were made of mild steels. The thickness and chemical composition of the surface oxide on fragments of the nails with surface oxides were also analyzed. The results indicated different contents of Fe and O in the oxide layer: a higher percentage of Fe was detected in the older nail compared with the more recent nail. Furthermore, the oxide layer thicknesses were significantly different: the average values were $378\ \mu\text{m}$ and approximately $67.3\ \mu\text{m}$ for the 1700s and 1600s nails, respectively. In both nails, the oxide layer was composed of only iron oxide; no other elements were

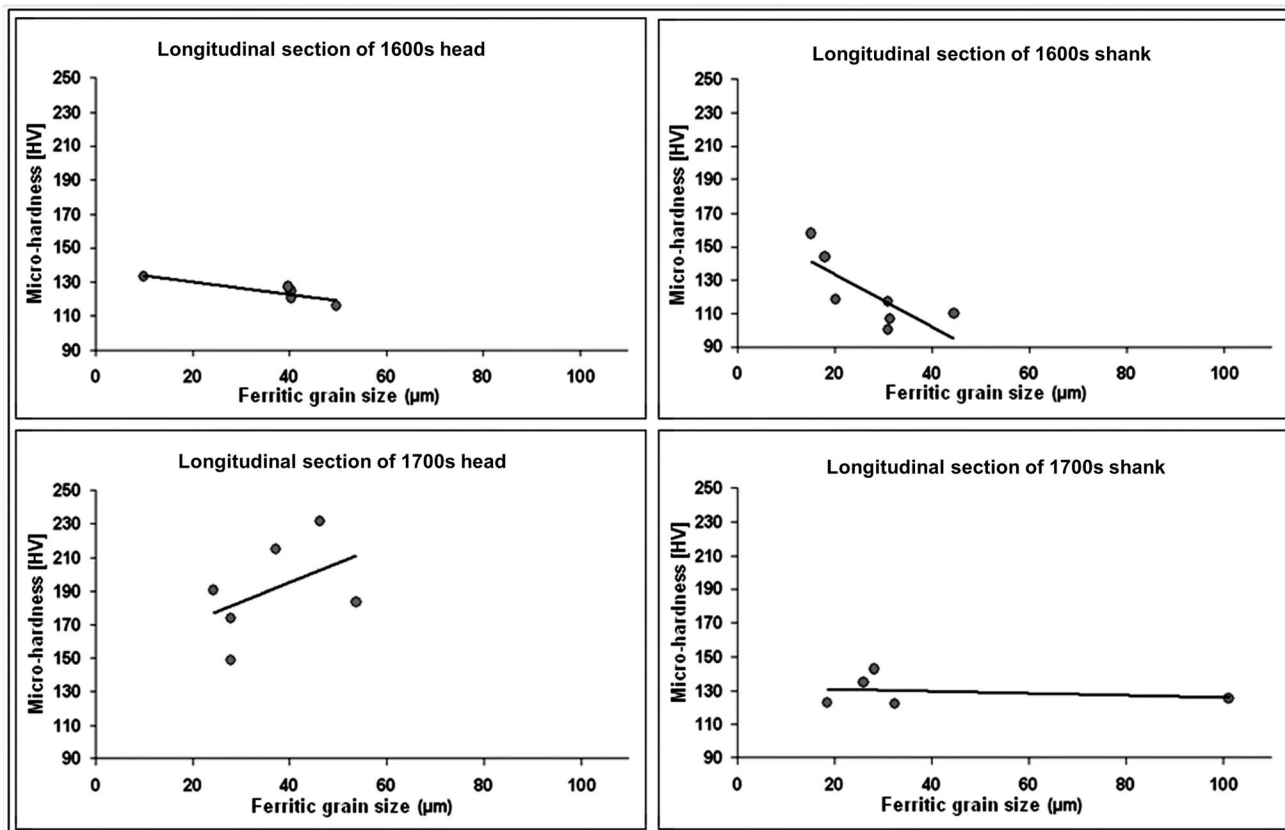


Fig. 5. Vickers microhardness with respect to the ferritic grain size in the longitudinal section of the nail shank and head.

detected via EDS. Figure 6a and b shows examples of these analyses.

μ XRD Measurements

μ XRD measurements were performed to examine the structural properties and to identify the crystalline phases of the nails. The measurements were performed on both the samples (to analyze the matrix crystalline phases) and the nail fragments (to investigate the external oxide phases). Figure 6a and b shows the Debye circles and the diffractograms of the samples and nail fragments, respectively.

The Debye circles for both nails were not continuous, and the signal for the 1700 s nail appeared to be weaker than that for the older one, confirming that the crystalline grains had different sizes, that they were differently oriented, and that the surface oxide layer in the 1700 s nail was thicker than that in the 1600s nail.

The μ XRD spectra of the nail fragments indicate that the external iron oxide phases were different between the two nails. In the older nail, magnetite and hematite were detected, whereas, in the newer one, wüstite was also detected. Additionally, the spectral analysis confirmed that the steel used for the nail production was mild steel; in fact, only alpha iron peaks were observed.

According to, Ref¹⁰ magnetite and hematite could be an index of the quality of the refinement process and the conservation status.

μ XRF Measurements

μ XRF measurements were performed to verify the SEM/EDS results, particularly with regard to the trace elements. The analyses were performed on the same samples that were used for μ XRD (as-polished samples and nail fragments with surface oxides). The results (Fig. S-4) confirmed the SEM/EDS analysis and revealed traces of elements, such as W and Cu in both nails, previously reported by quantitative analysis; this presence is probably owing to the iron ore used in the production process.

Nonmetallic-Inclusion Study Using SEM/EDS Analysis

A careful examination was performed using SEM coupled with an EDS microanalyzer to precisely characterize the nonmetallic inclusions in the nails. Through this analysis, the origin of the nonmetallic inclusions could be identified, and information regarding the production methods of the nails could be obtained. Semiquantitative chemical analyses, where the C content was neglected owing to the limits of the instrument for light elements, were conducted both as spots within each phase and as

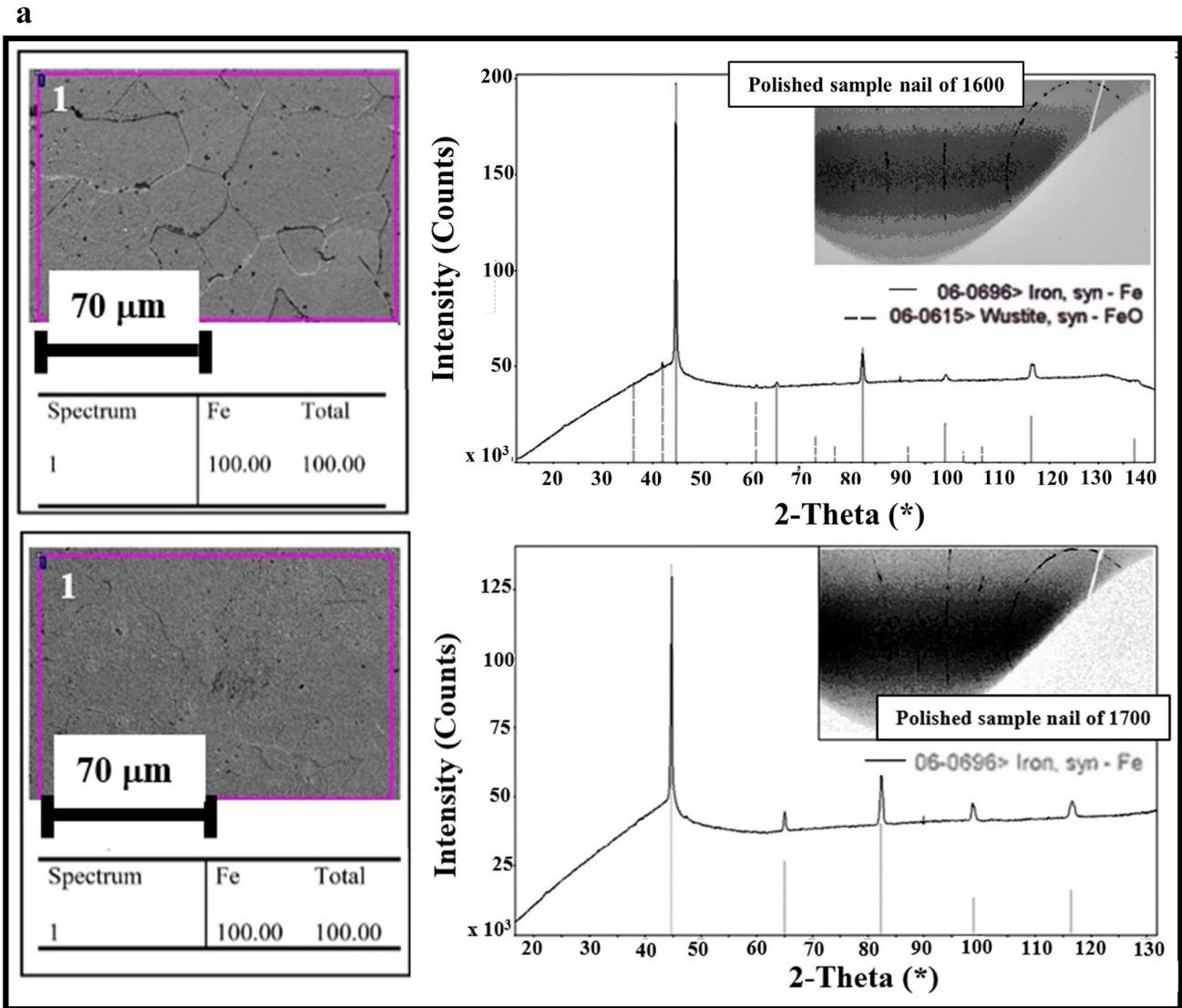


Fig. 6. SEM/EDS analysis and μ XRD measurements of the matrix and surface oxides for (a) the as-polished samples and (b) fragments of the nails with surface oxides.

the overall phase average, to gather reliable data regarding all the major inclusion constituents. The observed phases were rich in O and other elements, confirming that these particles were nonmetallic inclusions. Subsequently, the relative amount of each chemical element was transformed into the oxide percentage through stoichiometric formulas. Hereafter, the results of the SEM/EDS investigation are presented considering the effect of corrosion phenomena, particularly for inclusions close to the surface, which resulted in a very large amount of iron oxide.

Examples of SEM images with the chemical mapping and EDS analysis of the inclusions are shown in Fig. 7a. The average of every inclusion type is reported in the ternary phase diagram of FeO-SiO₂-CaO (Fig. 7b) to provide a rough indication of the temperature range reached during the

production process and for evaluation of the furnace efficiency.

The numerous nonmetallic inclusions present in the inner part of the nails exhibited a chemical composition and a morphology mainly attributable to the entrapped slag. Although both nails had a significant amount of inclusions, the concentration and number of inclusions were greater in the 1600s nail. In both nails, the inclusions tended to have a preferential orientation induced by the plastic-deformation processes. During the inclusion investigations, substantial differences were observed between the two examined nails. First, there were different welding lines in the 1600s nail that followed the whole length of the specimen and consisted of dark glass inclusions. The inclusion morphology suggests that the nail was manufactured in pattern-welded steel. These

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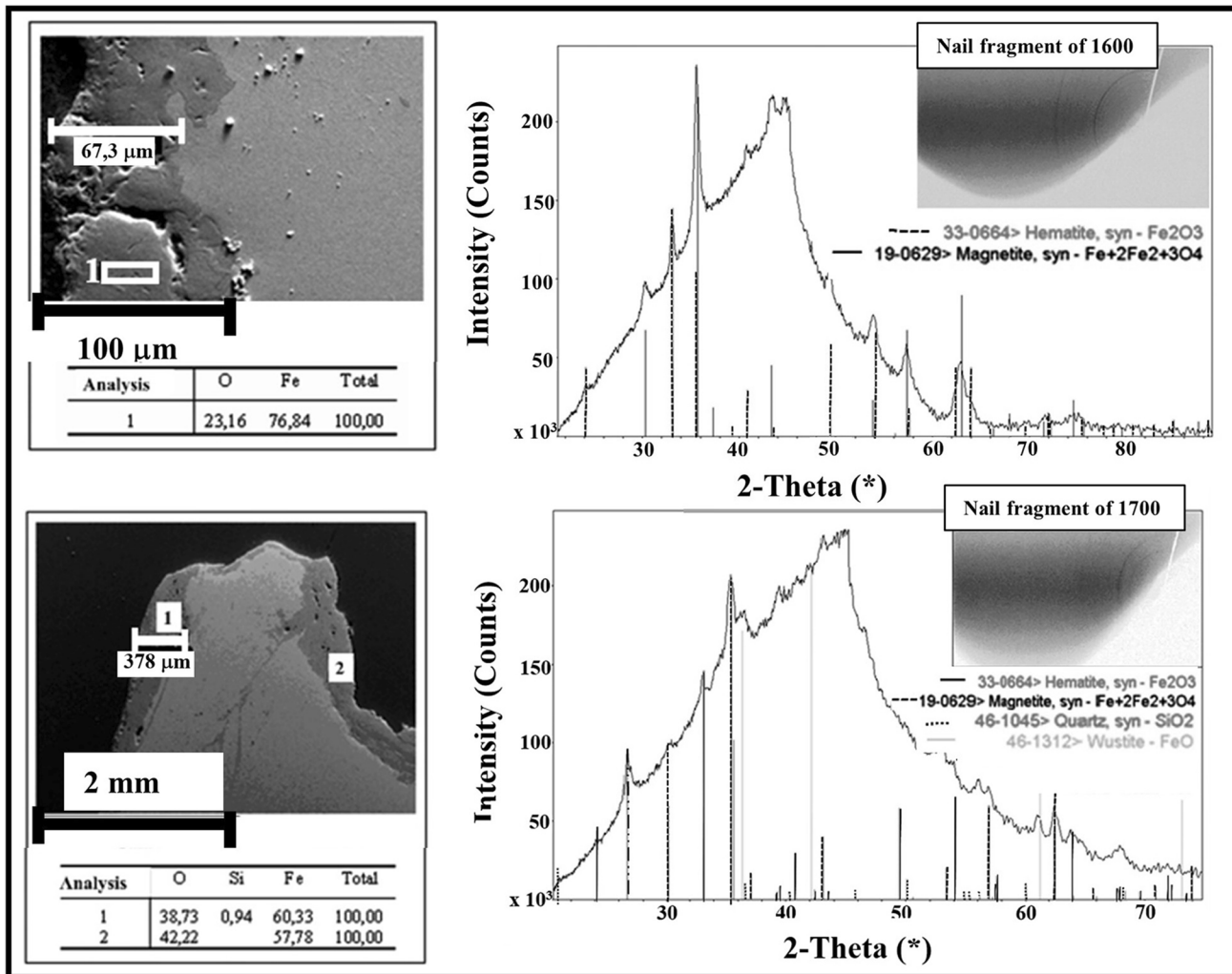


Fig. 6. continued

welding lines were not evident in the 1700s nail, which appeared to be produced from a single steel block. To support this hypothesis, the concentrations of elements constituting the oxides were examined, as follows. There was approximately twice as much Si in the 1700s nail compared with the 1600s nail. Mn, which was present only in trace amounts in the 1600s nail, had a concentration of approximately 10 wt.% in the 1700s nail. P was present only in some inclusions of the 1600s nail, and it was present in both nail matrices (ppm level). These observations allowed the identification of the different chemical compositions of the nonmetallic inclusions in the two nails. The inclusions in the 1600s nail were predominantly composed of wüstite and dark glass inclusions of the olivine type, such as calcic fayalite (a dark glassy matrix with light spots of a rich Fe phase) or kirschsteinite. These inclusions contained small amounts of Al_2O_3 , MgO , and P_2O_5 . It is necessary to highlight the significant presence of CaO not only in the fayalite inclusions

but also in some wüstite inclusions. Phosphorus oxide (P_2O_5), which was found only in the 1600s nail, being detected within the glassy inclusions; in this area, the microstructure was ferritic. The behavior of P is mainly controlled by temperature and by the acidity of the slag. Slags of high acidity (> 45 wt.% SiO_2) do not usually host P. Less acidic slags may contain as much as 10–100 times of P_2O_5 .¹³ The correlation between the P_2O_5 content in the slag and the matrix strongly depends on the Mn content and the forging temperature; in fact, during the smelting process, P can be reduced and, subsequently, owing to the oxidant atmosphere of the finery forge and long permanence, returned to the oxidized form and absorbed by lime.^{7,8} This evidence is in accordance with the two examined nails (refer to the FeO-SiO_2 diagram in Fig. 7c). The results suggest that the olivine-type inclusions, which were rich in calcium oxide, probably originated from a smelting or fining process, with a furnace temperature of at least 1200°C (Fig. 7b). In contrast, the

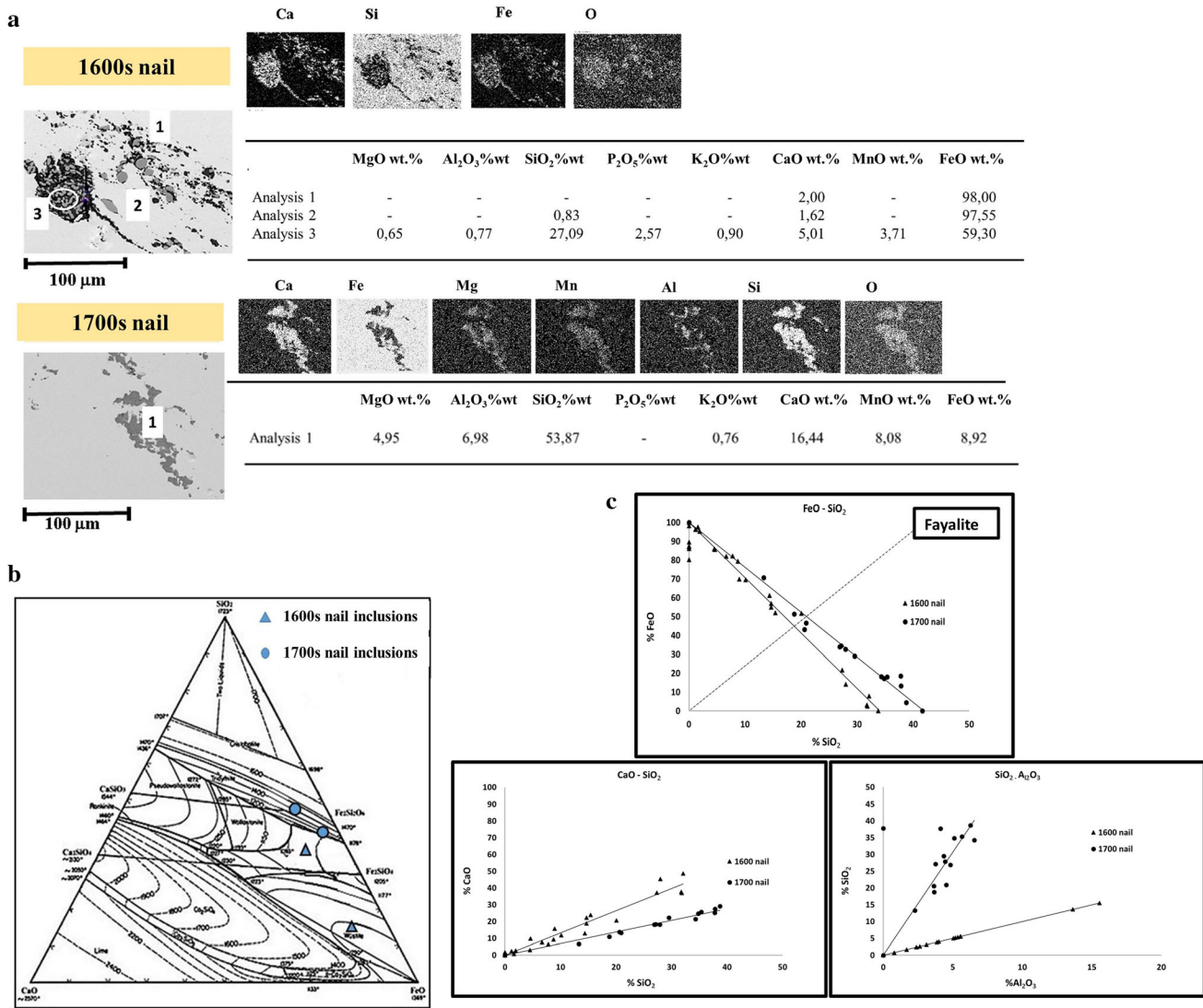


Fig. 7. Analyses of the nonmetallic inclusions: (a) SEM images with corresponding EDS chemical analysis and maps; (b) ternary phase diagram of FeO-SiO₂-CaO, indicating the average chemical composition of the inclusions; (c) correlations between different oxides.

wüstite inclusions were formed at temperatures of < 1200°C and probably originated from oxidation phenomena during smithing operations or from the entrapment of FeO scales formed during forging process. The excess amounts of Mg and Ca were due to their higher concentrations in the ore. However, another important explanation was proposed: perhaps the fluxing of the forge system was made with a Mg- and Ca-rich material.¹⁴ The presence of these inclusions indicates that the 1600s nail was produced in pattern-welded steel.

In the 1700s nail, the inclusions were principally composed of calcic fayalite and gray elongated glassy inclusions with fine fayalite precipitates and small amounts of Al₂O₃, MgO, and K₂O. These inclusions had high Mn contents, indicating a significant Mn content in the ore. In particular, the Ellingham diagram indicates that MnO is more stable than FeO, but the former oxide is partially

reduced in the iron blast furnace to form dilute solutions of Mn in the liquid pig iron. During this second stage of the indirect process, pig iron was little by little remelted under highly oxidizing conditions to form pure iron or carbon steel; Mn was first oxidized and eliminated within the slag.^{7,16} This last chemical composition suggests that the gray elongated glassy inclusions could be entrapments of the fluxes, which the ancient blacksmiths added in the fining operation after the reduction stage (during the forging processes) to cover the surfaces of the steel block for oxidation protection, or furnace refractory residuals. According to historical sources, these fluxes comprised mostly silica sand, glass powder, and lime.^{8,15} The observed glassy inclusions indicate that the temperature reached 1300–1400°C in some part of the furnace (Fig. 7b), and thus the melting temperature of the cast iron was reached. The correlations between

some oxides are presented in Fig. 7c. The most important relationship is that between FeO and SiO₂, the graph indicating a linear dependence between these two oxides, with the slope corresponding to the amount of impurities. If the amount of impurities is small, the line falls close to the 45° line toward 100% SiO₂; otherwise, the line falls toward a lower SiO₂ amount.¹³ The inclusions of the 1600s nail intercept the abscissa at a silica value of approximately 34%, while, for the 1700s nail, the value is 42%. These results confirm the superior cleaning and furnace efficiency for the more recent nail. The other oxide correlations are important because as the slag becomes depleted in FeO, the amount of oxides increases, but their ratios remain constant, as they are nonreducible compounds. These ratios are very important because they characterize the furnace, ore, and fuel utilized. According to the relationships presented in Fig. 7c, the two nails were not produced in the same melting/forging system.

CONCLUSION

The metallurgical and mechanical properties of two ancient iron nails (dated to the seventeenth and eighteenth centuries) found at a private estate in the village of Limone sul Garda (in Lombardy, Italy) were compared. First, the microstructural properties and hardness distributions were investigated, with a focus on the plastic-deformation flow lines. μ XRD and μ XRF measurements were performed to validate the quantometer analysis. Then, a careful SEM/EDS investigation of the nonmetallic inclusion types and distributions was performed. According to the results, the following conclusions are drawn.

- Both nails had a predominantly ferritic microstructure characterized by variable sizes and considerable directionality of the grains in different parts of the nails, which may be due to partial recrystallization during the plastic-deformation process used for nail production. The microhardness of the 1600 s nail varied between 100 and 158 HV, in accordance with the typical ferritic phase values. In contrast, the microhardness of the 1700s nail varied in the range of 122–232 HV. The highest hardness was observed in the head of the nail and was probably due to various concurrent hardening contributions (e.g., the presence of pearlite traces, small oxide inclusions in the steel matrix, a solid solution effect due to the higher P content, or the drastic plastic deformation in this zone). The microstructural analysis was confirmed by the quantometer results, which indicated that the nails were made of mild steel. μ XRD and μ XRF measurements supported the structural properties and the crystalline phase identified. The results of μ XRD and SEM/EDS analyses indicated that the surface oxide layer was thicker for

the 1700s nail than for the 1600s one. The spectra suggested that the surface iron oxide phases were different between the two nails. In the older nail, magnetite and hematite were detected, whereas, in the more recent nail, wüstite was also detected. Magnetite and hematite could be an index of the quality of the refinement process and the conservation status.

- Observations of the nonmetallic-inclusion morphologies, microstructures, and flow lines indicated different production processes for the two nails. The flow lines indicated that, in the 1600s nail, the head was probably obtained via shank bending, whereas, in the 1700s nail, it was probably obtained through compression stresses applied to the shank by a mallet or hammer. Additionally, the presence of different welding lines containing oxide particles in the 1600s nail suggested a production method involving the welding/hammering of bars. In the 1700s nail, there was no evidence of welding lines, and the nail appeared to be produced from a single rod. The presence of a coarser grain in the shank center may be due to the different forging reduction ratios between the surface and the bulk, confirming the aforementioned hypothesis.
- To complete the study, an inclusion examination was performed using SEM coupled with an EDS microanalyzer to precisely characterize the non-metallic inclusions in the nails and obtain further information regarding the production methods of the nails. Although both nails contained significant amounts of inclusions, the concentration and number of inclusions were greater for the 1600s nail. The single chemical elements were transformed into the oxide percentage through stoichiometric formulas, and it was found that the main compounds in the entrapped slag inclusions were different between the two nails. In particular, wüstite and dark glass inclusions of the olivine type (weld lines) were observed in the 1600s nail, whereas calcic fayalite and glassy inclusions were observed in the 1700s nail. Phosphorus oxide (P₂O₅), which was found only in the 1600s nail, was detected within the glassy inclusions. The behavior of P is mainly controlled by the temperature and acidity of the slag. The correlation between the P₂O₅ content of the slag and the matrix strongly depends on the Mn content and forging temperature; in fact, during the smelting process, P can be reduced and, subsequently, owing to the oxidant atmosphere of the finery forge and long permanence, returned in oxidized form and absorbed by lime. The significant presence of CaO and MgO was observed in the inclusions of both nails, and a high Mn content was observed for the 1700s nail. The excess amounts of Mg and Ca were due to their higher concentrations in the ore or in the fluxing added to the forge system.

- The detected compounds were reported in a CaO-SiO₂-FeO ternary diagram to provide a rough indication of the temperature range reached during the production process and to evaluate the furnace efficiency. The results indicated that the olivine-type inclusions, which were rich in calcium oxide, probably originated from a smelting or fining process, with a furnace temperature of at least 1200°C. In contrast, the wüstite-type inclusions were formed at temperatures of < 1200°C and probably originated from oxidation phenomena during smithing operations or from entrapments of FeO scales formed during the forging process. For the 1700s nail, the gray elongated glassy inclusions could be entrapments of the fluxes (i.e., silica sand, glass powder) and lime, with which the ancient blacksmiths covered the surfaces of the steel block to prevent oxidation, or trapped refractory residuals. The presence of glassy inclusions suggests that the temperature in the furnace reached approximately 1300–1400°C.
- The correlations between some oxides were reported. These relationships suggested that the two nails were not produced in the same melting/forging system and indicated the superior cleaning and furnace efficiency for the more recent nail.
- The differences in the nonmetallic-inclusion morphologies and temperatures suggested that different types of furnaces were used for the metal production. Moreover, the presence of Mn in the matrix of the 1700s nail may confirm this hypothesis. Mn is potentially a reliable indicator of smelting conditions, because it forms an oxide that melts at a high temperature. Thus, the presence of Mn supports the hypothesis that the 1700s nail was forged from a metal rod produced using a blast furnace. Here, a reduction of cast iron with thorough decarburization was performed to obtain a mild steel. Therefore, it is probable that the 1700s nail was obtained from a metal rod produced using the indirect process. In contrast, the 1600s nail was probably forged from a rod made by boiling an Fe sponge (blum) previously produced in a “bassofuoco” oven, followed by a direct process for iron production. This hypothesis supports the oxide bands oriented along the working direction observed in the nail shank and, particularly, in the nail head caused by the imperfect welding of the iron sponge layers during the rod forming.

Finally, with regard to the restoration of the lemon houses, it is worth noting that the restoration of ancient buildings aims to achieve a high level of authenticity, replicating materials and techniques as closely as possible. The results of the analyses carried out in this research provided new

information on the manufacturing processes of the nails found in one of these structures, showing that two different techniques were used. Therefore, nails similar to the original ones could be produced with the same processes in use 300–400 years ago and could be used during the restoration of the lemon houses in place of more modern nails in order to accurately recreate the form, features and character as the lemon houses appeared in the past protecting their heritage value. The knowledge of the production techniques of the nails used in the lemon houses is also important for the historical studies. Indeed, the production process is itself part of the heritage.

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ELECTRONIC SUPPLEMENTARY MATERIAL

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