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Archaeological Iron Conservation Colloquium 2010

Extended Abstracts

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Extended Abstracts

Session 2:

Iron Conservation Projects around the World

ABOUT CORROSION AND CONSERVATION PROBLEMS OF IRON ARTEFACTS COMING FROM ORADEA FORTRESS

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Introduction

The today Oradea fortress was built during the XVI-XVII centures. Ruins of buildings (the XIII-XVII centuries), artefacts and fragments (discovered during archaeological diggings 1991-2001, 2005-2007, 2009) are a great challenge for studyand conservation nowadays (Rusu et al. 2002; Muresan 2009). A special attention will be paid to the corroded iron artefacts.

General considerations about archaeological iron corrosion

"Rust" is associated with iron corrosion which in the language of chemistry is called oxidation. During the burial period the iron undergoes ionization as a consequence of the electrochemical phenomena: the anodic process consisting of iron oxidation is balanced by the depolarization process at the cathodic areas. The depolarization depends on the parameters of the environment.

It is generally known (Selwyn 2004) that the main phases of rust are oxides and oxyhydroxides such as: maghemite (γ-Fe_2O_3) magnetite (Fe_3O_4), goethite, α-FeOOH), and lepidocrocite γ-FeO(OH). In addition to the above mentioned corrosion products, other specific ones may be identified due to the particular soil/environmental composition/parameters (soil pH, soluble salts, aeration, soil constituents, and synergic effects).

Iron artefacts from Oradea fortress

The soil of the fortress may be considered near-anoxic and carbonated, because of a stone pavement from the 18th century that was found at a deeper depth than 20 cm and the other ruins of ancient buildings present there, too. Therefore, carbonates (Saheb 2007) were expected to be present. But things are not so simple: by means of ATR-IR [analysis realized at National Researching Institute for Conservation and Restoration, Bucharest with Bruker Experimental IR-ATR (Diamond, Helios XPM, 5000-400cm^{-1}, 4cm^{-1} resolution)], organic components (aromatic structures and probably oil), kaolinite, quartz, carbonates, and hydrated water were detected too. The heterogeneity of the soil caused a lot of problems in attributing the peaks and discriminating the components (for the iron corrosion components, too).

Now, speaking about the iron artefacts coming from Oradea fortress, each digging brought up hundreds of objects or fragments, with different degrees of mineralization and deformation,

even without possibility of being identified. Their conservation requires solving a lot of problems. Great battle, few weapons! A strategy may be a useful tool. It is important to acknowledge: which are the problems to be solved; which are the ideal requirements to conserve the discovered artefacts and the realistic ways/possibilities to do that. The problems to be resolved are the following: a lot of metallic artefacts were discovered during each excavation; the iron ones were corroded and mineralized (most of the artefacts looked fragile); the artefacts must be stabilized and conserved; no supporting expenses for the research of the artefacts. To divide the iron artefacts, from the beginnings (by examination tools), in categories based on their emergency degree and degrees of mineralization seems time gaining.

Some of badly corroded iron artefacts from Oradea fortress didn't lost the original shape. It is the case of a fragment of medieval steel armour that was cremated. Details of the morphology of the corrosion products were observed by optical microscope (magnification 50x, 100x). Spectral analysis was performed by ATR-IR on iron compound. Standard spectra were used. Goethite, lepidocrocite, iron oxide, calcite, were detected by both methods. But the research must to be continued (complementary and non-destructive tools are necessary (Neff et al. 2004).

Height surface sensitive techniques as IRRAS (infrared reflection absorption spectroscopy, QCM (quartz crystal microbalance) and TM-AFM (tapping-mode atomic force microscopy) were used (Kleber et al. 2007) for studying initial atmospheric corrosion of iron, copper and silver.

Now, topography data are linked to the chemical information on the same sample area. The Interdisciplinary and Experimental Research Institute from Cluj-Napoca is equipped with a WITec instrument, an Alpha 300A with Confocal Raman Alpha 300R, that offers the possibility to acquire non-destructive chemical information with a resolution down to the optical diffraction limits (200nm). All this sounds great! It makes the tool an ideal one! But there is a trap here! The surface of the artefact is a rough one and this equipment needs a smooth surface at a nanoscale level. For the moment, the tests made on an iron artefact sample, archaeological glass, polished bone have no significance. Then it is necessary to bring the sample parameters compatible to the equipment!

Final considerations

The conservation of great quantities of excavated iron artefacts needs particular management strategy. The examination methods are used on every artefact. Complex analysis is done to representative or particular artefacts. Samples of soil, corrosion products, and fragments of artefacts may be collected for further analysis. When new scientific tools are to be tested for studying the artefacts a first stage must be a detailed preliminary analysis.

The analysis techniques at nanoscale (molecular!) level may be used for a better conservation of artefacts. To "see" a molecular structure is a scientific success or an intrusion!?!

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IRON FROM LONDON'S WATERLOGGED SITES: ASSESSING THE OUTCOMES OF TREATMENT AND PASSIVE STORAGE

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In the 1980s, a number of conservation treatments were used on 'waterfront' iron at the Museum of London and elsewhere. Surveys of condition suggested that the iron objects that had been treated remained in good condition compared to objects that had not been treated. However, since 1990, active conservation treatments for iron have been largely discontinued in the UK. At the Museum of London this is largely due to changes to funding and project priorities, a minimally interventive approach to treatment and environmental issues regarding use and disposal of treatment solutions. However, the effect on ironwork of this approach has not been studied. The original aim of this work was to establish whether untreated iron from waterlogged contexts from the 1980s and 1990s in good desiccated storage had deteriorated since excavation compared to treated iron. By assessing several different sites using a standard statistical method, it is hoped that some conclusions can be made. However as this work progresses, the limitations of assessments of working archives have become apparent. This paper will also discuss these limitations.

The material and assessment method

The quality of iron objects from London's excavations with waterlogged conditions can be exceptional. Corrosion layers tend to be thin, conforming to the surface, and features such as plating, pattern welding, maker's marks, copper alloy, silver and tin inlays survive well. In contrast, iron from aerobic contexts normally has voluminous corrosion that obscures and sometimes destroys surfaces and features.

Fig. 1 Saxon blade with brass and copper alloy inlay, typical of the excellent condition of some iron from London 'waterfront' sites

The assessment currently has two parts:

- A reassessment of the condition of a group of 'waterfront' iron objects treated in the 1980s and assessed at regular intervals until 2000.
- Examination of 'waterfront' iron objects from sites that have had no active treatment, relying on passive storage in boxes with silica gel.

Assessments will use the Criterion Anchored Rating Scale (CARS) method to create statistically valid data. CARS was applied by Suenson-Taylor and Sully (1996) to archaeological leather and then adapted by Heywood in 2000 for the assessment of iron. CARS is based on the idea of interval data, that is measurement on a scale of equal intervals, eg length or weight, rather than ordinal data, which is a physical measurement that can be put into ranked order or counted.

Work in progress: assessment of untreated iron

At the time of writing of this abstract, the assessment of an untreated group from a 1990s excavation has been completed using CARS. This group of iron was chosen as it was thought to have received consistent desiccated storage in good archival packaging throughout its excavated life, with the intention of comparing it with treated material. The 741 objects from this one site ranged from pins to knives to styli and a large number of unidentified fragments or parts of objects. Nearly all the objects are packed in perforated clear polythene bags with Tyvek labels. The bags are stacked upright in a polythene box with a sealable lid and a bag of silica gel. The boxes are stored in a dehumidified store designated for metals.

It was found that 684 objects, that is, 92% of those examined had the highest possible CARS score. CARS does provide for some corrosion in its top score (up to 15% of the object affected by corrosion is acceptable within this score). As a result, it was decided additionally to get an indication of the proportion of these that have no corrosion at all. 134 objects were surveyed; 109 out of the 134 (over 81%) still had no active corrosion.

This demonstrates that most of the objects are in very good condition. This has been achieved, despite long periods when it was found that the desiccated environment had not been maintained over the 15 years since these objects were excavated. It had been assumed that we would be assessing a group of iron that had been in well-maintained silica gel storage for a valid comparison to treated material. However, when this material was retrieved it was found that a low RH (below 12%) could only be assumed for approximately half the time it had been in storage. This was due to periods of examination by finds specialists, illustrators and photographers, and a lack of staff resources to routinely maintain the gel. For the rest of the time it will have been stored in an environment of 30-40% RH and within that, short periods of several months potentially at higher levels when removed from store and not kept in silica gel.

Work in progress: assessment of treated iron

At the time of writing the group of treated material from the 1980s is about to be assessed. It will have been over 25 years since this material was treated; the condition of this iron has been tracked with regular assessments (Keene 1994; Heywood 2000).

Observations to date

With the pressures on budgets in both commercial archaeology and museums, it is essential to establish the effectiveness of treatment and storage regimes. For excavation archives in use (eg for assessments, illustration, research), and with limited staff resources, the reality is that it can be difficult to maintain the desiccated conditions recommended to slow down or halt corrosion. As a result, we do not have a group of untreated iron that can show the effectiveness of consistent desiccated storage. Nevertheless, the material examined to date has survived well despite no treatment and long periods out of desiccation.

We cannot claim the sites chosen to be statistically representative of all the excavated 'waterfront' iron in our stores, nor are we likely through this assessment to be able to isolate factors in the causes of good preservation for our 'waterfront' iron such as burial environment, treatment and length of time in desiccation. Reducing variables is difficult with 'real' material. However it does provide a starting point which we would welcome further researchers' assistance to better define. Stored material can provide an invaluable resource for reviews of treatments and storage methods if limitations are factored in.

This body of work is a result of a 'call to action' at a recent conference on iron (ICON Archaeology Group, *Archaeological Iron: Reflection and Outlook*, London, September 2009). Our assessments on 'real' material are intended to complement the experimental work in progress at Cardiff University, English Heritage and the British Museum. These studies are looking at optimum conditions for storage of iron, and the effectiveness of treatment in a wider body of UK material. It is hoped that the combination of experimental work and assessments of excavation archives will lead to significant and useful conclusions.

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THE KUR-PROJECT "LARGE QUANTITY FINDS IN ARCHAEOLOGICAL COLLECTIONS"

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The KUR-project – an introduction

Large quantities of finds – especially those consisting of archaeological iron and waterlogged wood– are always difficult to handle.

To tackle this challenge many different methods of dealing with these finds have been developed. The project wants to examine and compare these treatments with regard to practicability, costs and efficiency.

The three year project is funded by the Kulturstiftung des Bundes (German Federal Cultural Foundation) and Kulturstiftung der Länder (Cultural Foundation of the Federal States). Executing institutions are the Archäologische Staatssammlung München (Bavarian State Archaeological Collection, ASM) and the Römisch Germanisches Zentralmuseum (Roman Germanic Central Museum, RGZM) in Mainz. It stands under the direction of Prof. Dr. Rupert Gebhard (ASM) and Prof. Dr. Markus Egg (RGZM).

The materials are divided between the institutions – Waldemar Muskalla and Markus Witt-köpper work with wood at the RGZM whereas the authors (ASM) focus on iron.

General procedure

The treatments used so far include packing the finds in different kinds of foils, in some cases adding for example oxygen absorbers or desalination in solutions like alkaline sulphite (see references). The methods are roughly classified into two categories: Storage and desalination. The former has two focuses – the methods for initial treatment on site need to be quick and simple, those for long term storage can involve bigger equipment since this is usually executed in lab environment. The sample objects are taken from two sites: An early medieval burial ground in Steinheim near Dillingen, Bavaria, excavated in 1987. The second site is a settlement located at the Leisenhartfeld in Manching, Bavaria, dug in the first half of 2009.
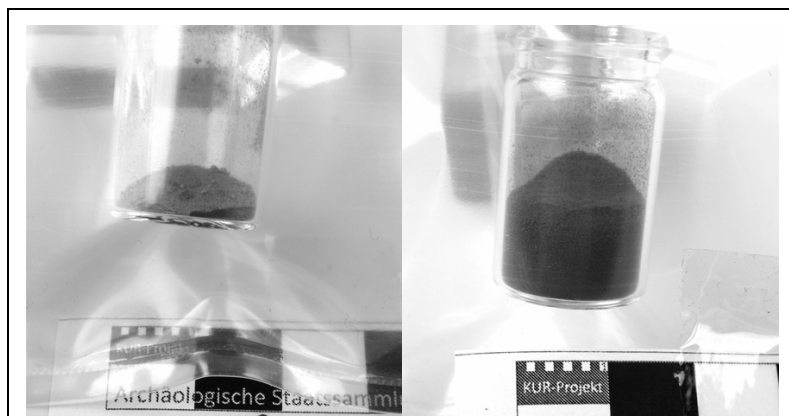
Fig. 1: Powder sample in the beginning and turned into akaganeite. **Photo: C. Mazzola, ASM**

An appropriate medium for testing the efficiency of the storage methods is a mixture of iron powder and iron chloride tetrahydrate (Guggenheimer 2006). Under normal climate conditions (ca. 25 °C, 40 % rH , 21 % O_2) this will turn into akaganeite after a few days (fig. 1).

Storage	Desalination
Different, preferably transparent foils (PE in several thicknesses, vacuum bags (PE/PA), ESCAL, aluminium barrier film),	Alkaline sulphite- or pure sodium hydroxide-treatment in different variations (vacuum, normal, different temperatures, etc.)
Different add-ons (oxygen absorber, silicagel, soil)	Heating in a dry environment (up to 200 °C)
Storage in a nitrogen filled case-system	Gas reduction
	Subcritical treatment (in Clemson, USA)
	Washing in distillied water in overpressure
Table 1: Overview of tested methods	

All samples are regularly weighed and photographed, objects x-rayed. For the oxygen monitoring a non-invasive oxygen meter is available. The progress of desalination baths is controlled by titration.

For the identification of the different iron minerals x-ray diffraction (XRD) and Moessbauer spectroscopy are used.

An overview of the tested methods is listed in table 1. Most tests were done under laboratory conditions. Some of the objects however have been packed on site in Manching by the excavation staff to see how the handling of foils and equipment fits in the routine.
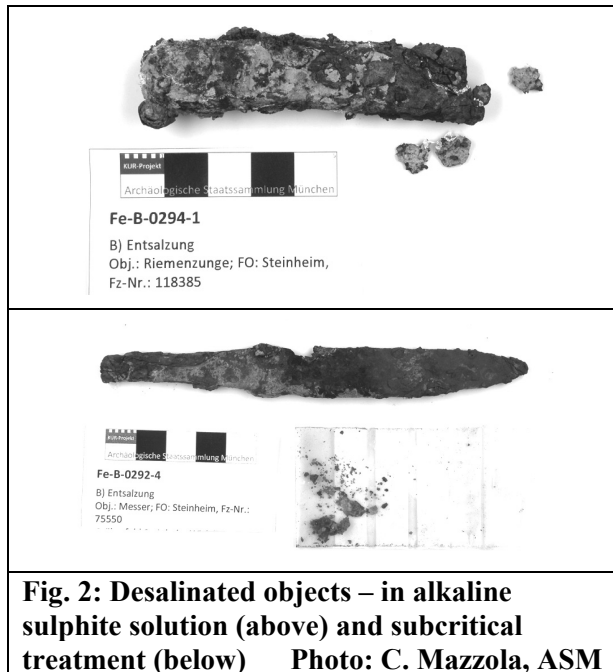
First observations

Looking at the storage options it was of little surprise that the PE-bags usually used on excavations offer only little protection against oxygen. The ESCAL foil holds tight as long as it is not strained extensively. Household vacuum bags seem to be an acceptable alternative – at least for a few months.

The conversion into akaganeite – indicated by weight and volume increase and colour change – seems to start already at oxygen levels as low as 1 %. It showed that with both powder and object samples the oxygen level drops after a while independently from the presence of an absorber. Probably the oxygen is used up in the oxidation process.

The tests on site were a mixed success. It was criticised, that the packing methods used were time consuming and that a 'packing person' would need to be budgeted from the start. A time and material saving alternative would be not to bag every single find in high quality foil.

Instead the finds of the day could be packed in a few bigger bags in the evening. Package on site however is generally advisable and should be considered when planning further excavations.

For desalination the suggested bath changing rhythm (3 or more baths à 3-4 weeks; Schmidt-Ott & Otto 2006) seems to be confirmed by the titration results.

Fig. 2: Desalinated objects – in alkaline sulphite solution (above) and subcritical treatment (below)   Photo: C. Mazzola, ASM

It appeared that the objects from the sodium hydroxide baths were a bit less brittle after the treatment than the alkaline sulphite objects.

Two objects have been sent to Clemson, USA for subcritical treatment. A moisture chamber test and analyses in Clemson and Munich point to a good desalination success. The main difference to finds which have been treated in alkaline sulphite solutions is a thin deep red layer of powdery hematite on the surface. However there was no distinction in the subsequent exposing of the 'original surface'.

Future prospects

Much remains to be done – more desalination variations, e.g. with the in the ASM available gas reduction machine. Improvement of the packing methods to make them quicker and a broader research in the foil sector are planned to find cheaper alternatives to ESCAL-foil. At present the systematic study of storage in nitrogen filled case-system has started.

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METALLURGICAL PROPERTIES OF STEEL USED IN A TRADITIONAL JAPANESE MATCHLOCK GUN
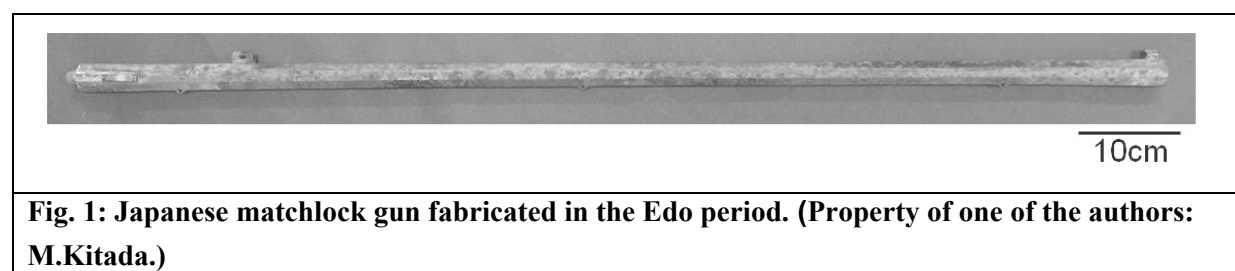
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Introduction

The microstructures, nonmetallic inclusions and mechanical properties of a steel barrel of a traditional Japanese matchlock gun fabricated in the middle of the Edo period (17th-18th century) have been investigated. Guns were introduced into Japan in the 16th century by Europeans. It is said that steel made from domestic iron sand and/or imported steel was used as the raw material of the barrel. However, the details have not been clarified yet because of the limited number of investigations. It is considered that the barrel of a Japanese matchlock gun was made mainly by hot forging, although the detailed fabrication technique of the barrel is not clear as it was carried out in secret. The purpose of this work is to obtain materials-science data of the raw materials of the Japanese matchlock gun and to investigate the fabrication technique of the steel barrel.

Experimental methods

The barrel used for analysis is shown in Fig.1. It is considered to have been made after 1624 from the shape of the sight. Specimens are cut from the center of the barrel. The carbon concentration is determined by chemical analysis. The metallurgical microstructure and nonmetallic inclusions of the barrel are observed using an optical microscope, a scanning electron microscope (SEM) and a transmission electron microscope (TEM). To observe the metallurgical structure, specimens were etched with 5% nital after being buffed with cerium oxide. The small-area concentration of a nonmetallic inclusion is obtained by electron dispersive X-ray analysis (EDS). The mechanical properties are evaluated by tension and hardness tests. To check the impact of fabrication (forging), a test piece is annealed (700°C x 1h) in inert atmosphere.

10cm

Fig. 1: Japanese matchlock gun fabricated in the Edo period. (Property of one of the authors: M.Kitada.)
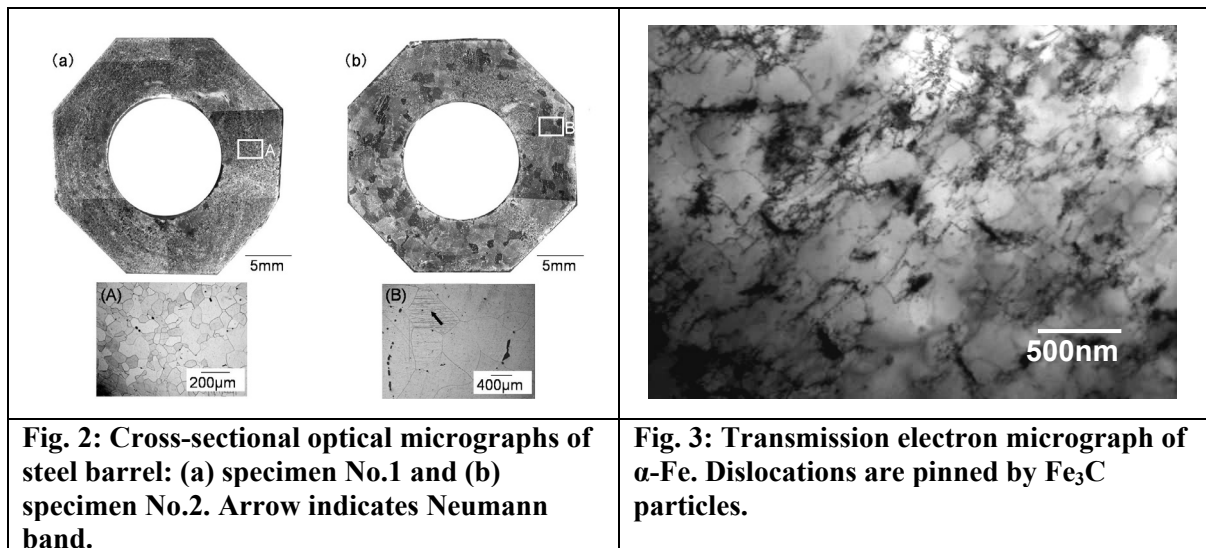
Results and discussion

1. Microstructures

The center of the barrel is made of mild steel containing 0.01-0.1 mass% carbon. Cross-sectional optical micrographs of specimens No.1 and No.2 are shown in Fig.2. Although specimens No.1 and No.2 both consist of α-Fe, the grain size is variable. The grain diameters of specimens No.1 and No.2 are 30-200μm and 200-1200μm, respectively. The metallurgical microstructures of a cross section parallel to the barrel and a surface show the same characteristic. The following two causes are considered to be responsible for the grain diameter variation: Firstly, the characteristics of the raw material (steel sheet) of the barrel itself and, secondly, the effects of the forging process, such as annealing temperature and annealing time.

A typical transmission electron micrograph of α-Fe is shown in Fig.3. Since many dislocations are observed in the crystals and pinned by Fe$_3$C particles, the steel was slightly forged at room temperature after hot forging.

Fig. 2: Cross-sectional optical micrographs of steel barrel: (a) specimen No.1 and (b) specimen No.2. Arrow indicates Neumann band.

Fig. 3: Transmission electron micrograph of α-Fe. Dislocations are pinned by Fe$_3$C particles.

2. Nonmetallic inclusions

Two typical microstructures of the nonmetallic inclusions are shown in Fig.4. Fe, Si, Al, Ca, K, Mg, P, Na and Ti are detected from nonmetallic inclusions of the barrel. Most Japanese iron sands contain Ti as ilmenite (FeTiO$_3$), but Japanese iron ore and imported steel do not contain Ti. Since Ti is detected, it is concluded that iron sand was used to make the steel.

The distributions of nonmetallic inclusions in the cross sections normal to the barrel and parallel to the barrel and surface are shown in Fig.5. From the distributions of nonmetallic inclusions in two typical Japanese barrels (Fig.6), it is concluded that the barrel was fabricated by the joining of two long edges of a steel sheet, which is called *Udonbari* (in Japanese: seamed steel pipe).
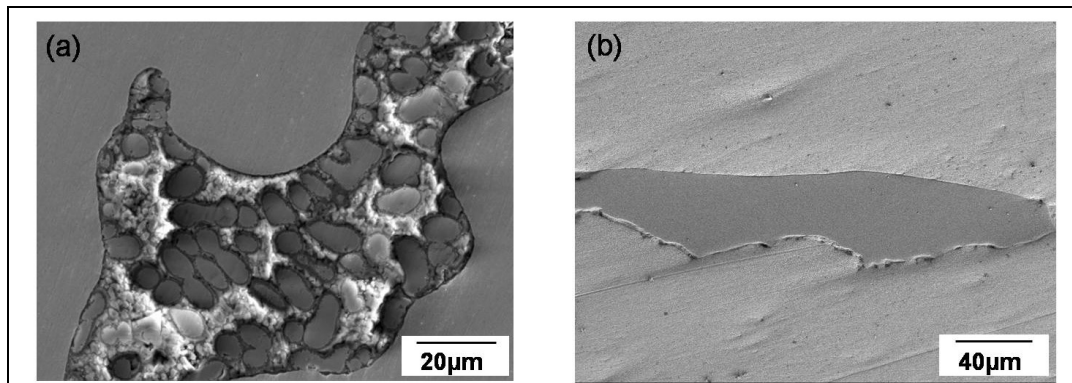
Fig. 4: SEM images of two typical microstructures of the nonmetallic inclusions, (a) FeO + Fayalite + glass matrix and (b) glass single phase.
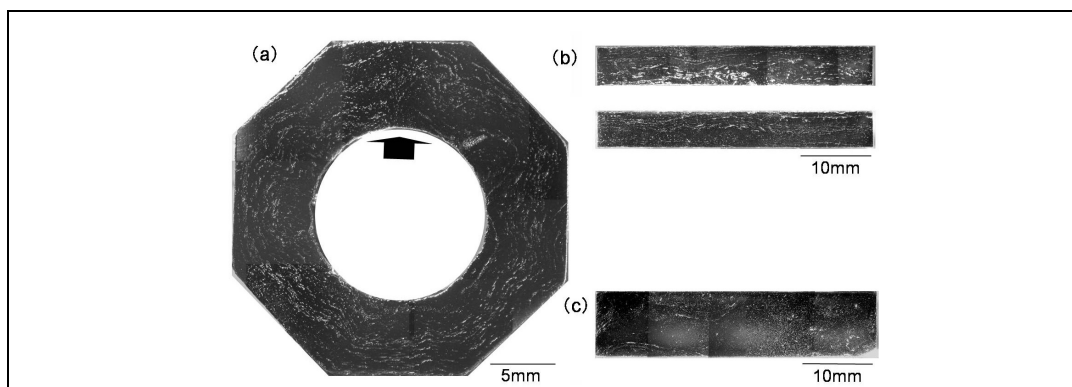

Fig. 5: Distributions of   on-metallic inclusions in (a) cross section normal to the barrel, (b) cross section parallel to the barrel and (c) surface. Arrow indicates assumed weld area of steel barrel.

Fig. 6: Schematic illustrations of distribution of nonmetallic inclusions (arrows: dotted lines) in the steel barrel of a Japanese matchlock gun: (a) *Udonbari* and (b) *Kazuramaki*.

3. Mechanical properties

The maximum Vickers hardness and tensile strength are 132Hv and 366Mpa, respectively. The values are slightly higher than those of the standard data of annealed mild steel; therefore, there is a possibility of work hardening by cold forging. Optical micrographs of the specimens before and after annealing are shown in Fig.7 and Fig.8. Crystal growth was observed after annealing. The maximum Vickers hardness and tensile strength are decreased by annealing at 118HV and 325MP, respectively. As the grain size and Vickers hardness of the surface change more markedly than those of the cross section, it is concluded that the steel was forged at room temperature after hot forging.
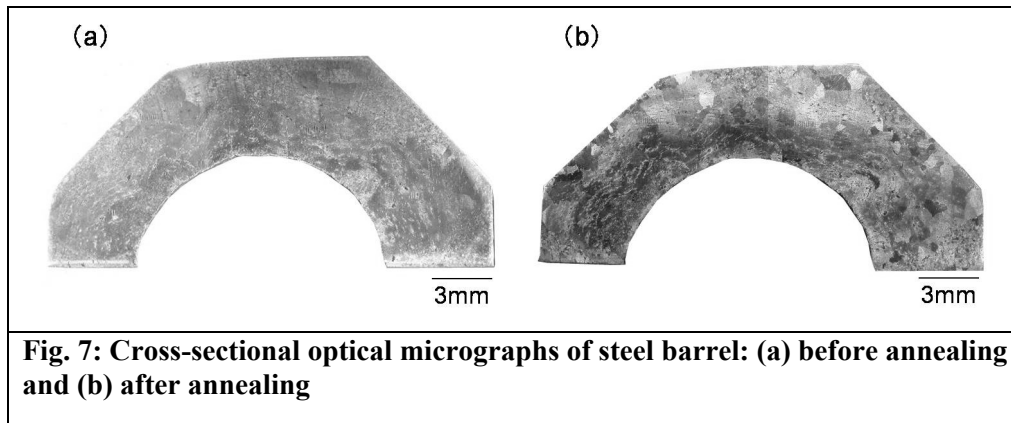
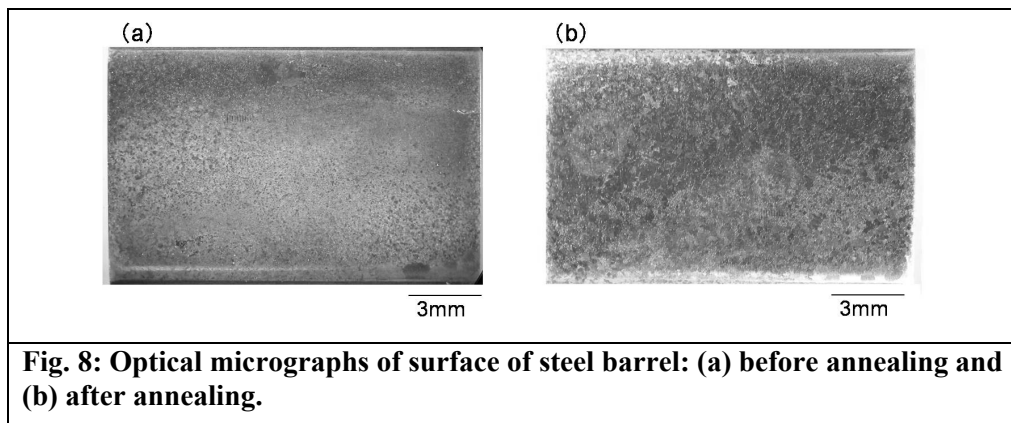**Fig. 7: Cross-sectional optical micrographs of steel barrel: (a) before annealing and (b) after annealing**

Fig. 8: Optical micrographs of surface of steel barrel: (a) before annealing and (b) after annealing.

Conclusions

The microstructures, nonmetallic inclusions and mechanical properties of the barrel of a Japanese matchlock gun were investigated. The center of the barrel is made from a mild steel that contains 0.01-0.1 mass% carbon. Since Ti is detected, it is determined that the iron sand was used as the raw material of the barrel. The barrel was fabricated by the hot-forge welding of a long steel sheet. The barrel was forged at room temperature after hot forging.

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IRON AND THE MICROSCOPE

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Ferrous materials have a long history in the crucial stages of development of metallurgical microscopy. The realization that Anglo-Saxon sword blades from Scandinavian excavations in the 19th century, were fabricated from pattern-welded iron of different kinds, spurred investigation and fascination with iron's past and the achievements of the blacksmith. At the same time, scientists were making significant advances in trying to prepare iron artefacts to examine microstructure, and explain the kind of products being produced, as well as understanding the microstructural reasons for the different behaviour of cast iron, steel and wrought iron. Observations on the structure of iron began in the 17th century, but the development of metallurgical microscopy began with the work of Henry Clifton Sorby in the 19th century, which has been reviewed in detail by Smith (1988).

In the Old World, iron was never molten in antiquity, except in small amounts, and was joined by welding or forging of pieces of iron together. As a result, the microstructure of iron is variable, due to weld lines, different carbon contents, and slag inclusions, and these differences are very informative concerning the processes of fabrication which have been employed to produce different artefacts (Smith 1981, Craddock 2005). Carbon content, methods of heat-treatment, extent of corrosion and patination can all be investigated with the microscope, which is part of the reason why conservation measures seek to preserve as much of the original object as possible for future scientific work. The improvement in conservation methods means that we can examine the microstructure of finds from excavations without the fear that they have been altered by treatment as they once might have been. Numerous conservation measures used to conserve iron in the past have failed to maintain the microstructural integrity of the material we were supposed to have preserved. Such techniques as heating iron artefacts to dull red heat, the older plasma reduction processes which used high temperatures, from 300-450 ^{o}C, hydrogen reduction and even electrolytic reduction not only stripped away all of the corrosion products in the case of the latter but altered the microstructure of the ferrous material being conserved in the case of the former. Our concern for metallurgical veracity is a major influence on conservation strategies. This veracity can be determined by microscopical examination, by x-ray radiography and by new non-destructive methods such as time-of-flight neutron diffraction analysis, used on a Song Dynasty Chinese iron coin (Huang et al 2010) to determine phase composition. The different phases of the iron-carbon system are very sensitive to fabrication techniques and compositional variations in carbon content.

In this short review of structure, we will examine some typical microstructures of ancient iron artefacts: wrought iron, low-carbon steel, high carbon-steel, welded structures, quenched martensite, tempered martensite, grey cast iron and white cast iron. The iron-carbon phase diagram is an essential backdrop for ferrous metallurgy which will be briefly examined, and which helps to define the phases of ferrite, austenite, ledeburite, pearlite, cementite and graphite. Even low contents of carbon, 0.4% , create remarkable changes in the properties of iron artefacts. Phosphoric iron was also an important product and occasionally nitrogen created nitrides, hardening the iron produced. Phosphoric iron creates possible contrasts with low-carbon steel used in pattern welding. Even in the bloomery process, small amounts of high carbon products, such as grey or white cast iron could be made, although the usual challenge was to retain or get enough carbon into the iron to create steel (Craddock 1995). The Chinese and Indian task was to remove enough carbon from cast iron products to produce steel. The co-fusion of wrought iron and cast iron was one way in which this could be done, used for one of the Indian crucible steel processes (Bronson 1986), or cast iron could be decarburized. The Chinese production of cast iron two thousand years before the Old World could make it in any quantity, resulted in a unique metallurgical development of grey cast iron, white cast iron and mottled or spheroidal graphite cast iron whose ferrous microstructures are often the most difficult to decipher in the corroded state. Diagrams which plot the changes of phases depending on the speed with which steels are quenched, known as time-temperature-transformation diagrams, are useful in determining the presence of the phases, bainite, troostite, martensite and other carbides (Rollason 1973). An example of a Japanese sword blade which shows martensite, troostite and the transition to fine pearlite and a lower carbon steel core will be discussed (Scott 1991). Hardening steels by quenching and tempering gave rise to products which were far superior to the copper alloys of the Bronze Age. Some of these products will be reviewed here, employing the metallurgical microscope and polished and etched sections of some of the iron artefacts examined in the laboratory.

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