Phase composition mapping of a 17th century Japanese helmet

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Abstract

Neutron Diffraction represents the ideal technique for the characterisation of the micro-structural properties of ancient metals, allowing to retrieve information on the smelting process, and the mechanical and thermal treatments applied during the manufacture of the sample.
The object under investigation is a 17th century Japanese helmet (*kabuto*) from the Haruta School, that has already been analysed, along with other six similar examples, using a general purpose neutron diffractometer. Through this study, the quality of the steel(phase composition) was determined and information on the thermo-mechanical treatments applied were inferred, averaging over a scattering volume that affected the entire thickness of the sample. The Haruta *kabuto* stood out for its very high carbon content, the absence of texture and residual strain, and very big grains size. These factors and the presence of incomplete reduction of the ore sand suggests the presence of plates with a composite structure of layers of steel and iron superimposed.
This paper shows the possibility of using neutron diffraction on a highly collimated instrument, such as ENGIN-X (ISIS, UK), to be able to select a very small gauge volume and, this way, to detect variations in the phase composition along the thickness of the plates.
Here we present novel results from diffraction measurements by using the instrument ENGIN-X. This study completes the previous cycle of neutron measurements on this sample and sheds light on the structure of the plates.

Keywords Neutron diffraction · Phase analysis · Quantitative analysis · Steel metallurgy · Carbon content · Japanese helmets · kabuto · Archaeometallurgy

Introduction

The armour and the sword of the samurai have long been considered to be objects of absolute beauty, from both an aesthetic and a technological point of view. The production of the traditional Japanese armour dates back to the 4th century A.D. and starting from its appearance on the battlefield it underwent several developments [1]. In the 15th century, the Japanese helmet (*kabuto*) became one of the most important elements among an armour's constituents since it allowed the samurai to stand out in the battlefield at a time when large armies of foot soldiers were becoming more common and fighting on horseback was in decline. From the second half of the 16th century, with the introduction of firearms, the construction technique and style of Japanese armourers changed to increase the protection offered by the armours and helmets [1]. This brought to the production of simple and sturdy armours that could be mass-produced to supply the demand from the internal conflicts between rival provincial states (Warring States Period, c. 1467 - c. 1603) that affected Japan until the early 17th century (see Fig. 1). For this reason, suites of armour with single metal plates (*tosei gusoku*, 'new armours') were preferred to lamellar ones (*yoroi*) that characterised the previous period.

With the decline of the samurai class in 19th century, Japanese armours became objects of interest to world collectors. Many examples now reside in museums and private collections allowing us to admire objects that are usually in excellent conservation status. Therefore, traditional analysis is not suitable for rare and unique objects of high scientific and cultural value.

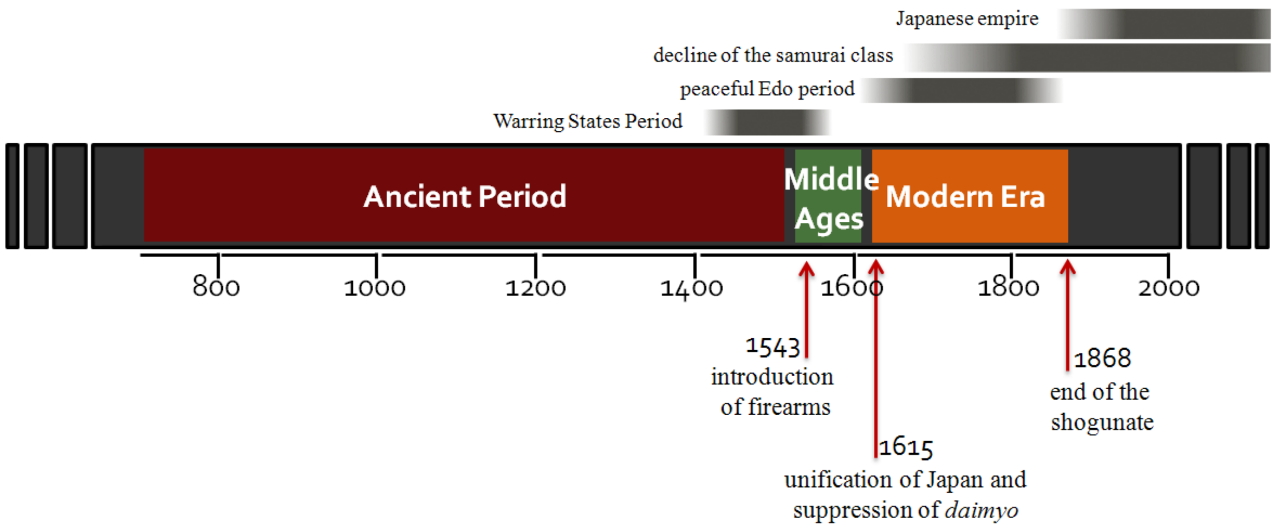

Fig 1 Outline of the evolution of armours in Japan with respect to the main historical events. Armours present different characteristics, depending on period of manufacturing; we can distinguish three periods: Ancient Period (*jōdai*; VIII century-1532), Middle Ages (*chūko*; 1532-1614), and Modern Era (*kindai*; 1614-1868) [1]. During the Ancient Period armours were built following principles of practicality and utility, without neglecting purely aesthetic features, such as gilding and decorative rivets in relief. Around the 10th century, the box-like *o-yoroi* appeared, an armour made of varying-sized strips of lamellae or iron plates, held together by silk lacing. Armours from the Middle Ages were characterised by a better wearability and provided better protection from the newly introduced firearms. The old lamellar armours were substituted by plate armour constructed from iron and steel plates. In the Modern Era, Japan entered the peaceful Edo period, samurai continued to use both plate and lamellar armour as a symbol of their status but traditional armours were no longer necessary for battles.

For these reasons, a non-invasive approach was carried out for the study of the metallurgical properties and phase composition of the sample. Time of Flight Neutron Diffraction (ToF-ND) represents one of the most suitable non-destructive techniques for the characterization of the microstructure of metal archaeological artefacts, because of the high penetration power of neutrons, even through thickness of several centimetres [2].

In this paper we will concentrate on a Japanese helmet from circa 1600, see figure 2, belonging to the Haruta school, which represented the most important armourers family of Japan and became official suppliers to the Shogun and the Imperial family until the end of 18th century [1]. The *kabuto* has already been studied using ToF-ND [3]. With this technique it is possible to gather information on the microscopic structure of samples (e.g. phase composition, texture, residual strain distribution), shedding light on the likely working techniques and on thermal treatments applied [3].

Fig 2 (left) Haruta *kabuto* (circa 1600) of *hari bachi* style, a multi-plate Japanese helmet bowl with no ridges and with filed flush rivets. (right) The helmet is signed “Haruta Yoshihisa saku” (Yoshi armourer of Haruta School). Within this school, the *hari-bachi* helmets stand out as being among the finest items produced. This helmet was formerly part of the H. Russell Robinson Collection [4].

Here we present novel results from diffraction measurements by using the instrument ENGIN-x (ISIS,UK). This study pushes the previous neutron investigations even further, allowing to shed light on the last unresolved questions concerning the structure of the plates[3]. In fact the results obtained from the preceding ToF-ND analysis suggested the presence of a composite material made of steel and iron superimposed. Although the metallographic study of Japanese armours is very limited with respect to the European ones [5], it seems in fact that some high quality Japanese armour plates were forged creating such composite structure. According to literature, the only example of such a structure has been revealed through metallography on an armour plate [6], but never on helmet plates.

Iron and steel smithing process in Japan

In Japan, the traditional smelting process of iron and steel occurred in the *tatara*, a clay furnace that incorporated bellows and had to be destroyed after the use for collecting the *kera*, a 2-2.5 ton of spongy “bloom” containing steel [7]. The temperature reached in the furnace ranges 1200-1500°, thus the metal was never completely melted. Due to the large dimensions of this furnace, the temperature reached was different depending on the height. This allowed the production of different types of iron, with varying degrees of carburization: wrought iron (*hocho tetsu*) at the top of the *tatara* where the temperature was the lowest; cast iron towards the middle; and hypereutectoid steel (*tama hagane*) at the bottom [8]. Once the *kera* was cooled, it was broken into small pieces, helping the selection of the desired portion of high- and low- carbon parts [9]. This procedure was fundamental in the forging of the famous katana, but it seems that it was also applied for creating high quality suits of armour.

Since 16th century, iron and steel plates were produced through a procedure called *jumonjikitae* (see Fig. 3), which is described by the 18th century Japanese author K. Sakakibara [1]. This process was repeated a minimum of ten times for iron (*namagame*=non refined iron) which was very rich in slug (about 2 wt. %), while for steel (*hagane*) it should not have been repeated more than five times in order not to lower the carbon content and reduce the hardness. Although the chemical transformations involved were unknown to them, this procedure was very effective for distributing the carbon content more evenly, and also reducing the size of the slag inclusions. The cross grain pattern deliberately created through *jumonjikitae* probably roots back in the wood technology, where composite materials are created to improve strength and stiffness, by cross-orienting highly anisotropic layers. The same result does not apply to metals, where a high temperature process, such as that required to forge weld together the different layers, anneals the metal and cancels previous deformations (as preferred grain orientation), determining the impossibility of reproducing a well defined cross-oriented material. In fact, during annealing the microstructure of the deformed metal undergoes a sequence of consecutive and overlapping stages as, recovery, re-crystallization, and grain growth [10]. Still, thanks to the composite structure and the presence of steel, such plates offered a very high level of protection and were able to resist arrows, missiles, and cutting blows [1].

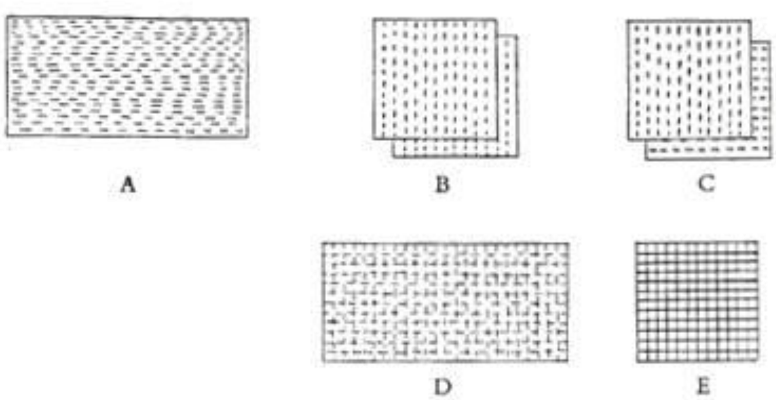

Fig 3: Sketch describing the *jumonjikitae* method for forging armour plates [1]; the hatching indicates the grain pattern of the metal. A block of metal was elongated into a metal sheet (A), cut into two squares and forge welded maintaining the same orientation of the grains (B). The block was then heated and hammered another time, elongating it again into a sheet. This was cut in squares and the two halves were transversely superimposed and forge welded (C), then hammered into a plate with the desired cross grain pattern (D). The armour plates were then forged welding together two layers of *tetsu* (a generic term including all kinds of iron and steel) superimposed, with steel on the outside and iron on the inside, alternating the grain direction of the two sheets (E).

Case study

The Haruta helmet was already analysed through neutron diffraction using the INES beamline (ISIS-UK) [11], evaluating the quality of the steel (i.e. the carbon content level), the present conservation status, and its microscopic properties [3]. During this study, the entire thickness of the sample was probed in two measuring points: on the front plate, and on the visor, as shown in figure 4.

Fig 4: Picture indicating the measuring points (circa 2.5x2.5 cm^2) for the INES diffraction measurement.

Considering the results obtained [3], the presence of a composite structure of steel and iron superimposed was suggested. Since no goethite or hematite was detected, we assumed that the presence of wüstite (0.7-1.0 wt. %) derives from an incomplete reduction of the ore sand. Magnetite (1.5-2.2 wt. %), on the other hand, could either be ascribed to the incomplete reduction of the ore or to an intentional bluing process of the surface. This method was used to create a patina called *sabi-tsuke* to prevent the tendency of steel to rust [12] The high level of cementite observed (up to 5.6 wt. % ≈ 0.4 wt. % of C) suppose a slow carburising process –in order to let the carbon diffuse into the matrix- that is incompatible with the presence of unreduced ore. On the other hand, the almost complete absence of fayalite is indicative of the labour of an experienced smith [13], that reached a good level of refinement with respect to slag inclusions.

A composite structure of layers of soft iron and steel, with wüstite in the former and cementite in the latter, would explain the data obtained. In support of this hypothesis, there is the total absence of texture, the very low residual strain, and the average presence of very large grains, indicating that the sample was subjected to an annealing treatment or to a high temperature process, such as that required to forge weld together layers of iron and steel.

The previous ToF-ND measurement probed the entire thickness of the material and did not distinguish whether the structure is composite or not.

Experimental set-up

The experiment was carried out at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, Oxford, UK) using the diffractometer ENGIN-X [14].

In neutron sources with a time structure the Time of Flight technique can be applied [15]. From the measurement of the time-of-flight (ToF) and scattering angle (Θ) it is possible to know the velocity of the neutrons and therefore their wavelengths. The Bragg's law can be then re-written as a function of the ToF of neutrons scattered from a set of planes of the sample d_{hkl}, as:

$$ToF_{hkl} = \left(\frac{2m_n}{h}\right) L \cdot d_{hkl} \cdot \sin\theta$$

Where m_n is the mass of the neutron, L is the total flight path of the pulsed beam from the moderator to the sample position, and Θ is the fixed scattering angle. So the d-spacing is obtained from the position of the ToF_{hkl} of the peak in the TOF spectrum.

ENGIN-X is an instrument dedicated to the study of the presence, amount, and direction of residual strains, on typical gauge volumes of few cubic millimetres. This is achieved through a collimation system both on the incident beam and in front of the detectors, so that only neutrons scattered from the desired gauge volume can reach the detector system. Scattered neutrons are recorded by two banks (Fig. 5) containing 1200 detectors each, and placed at 90° on the sides of the sample position, 1.5 m apart.

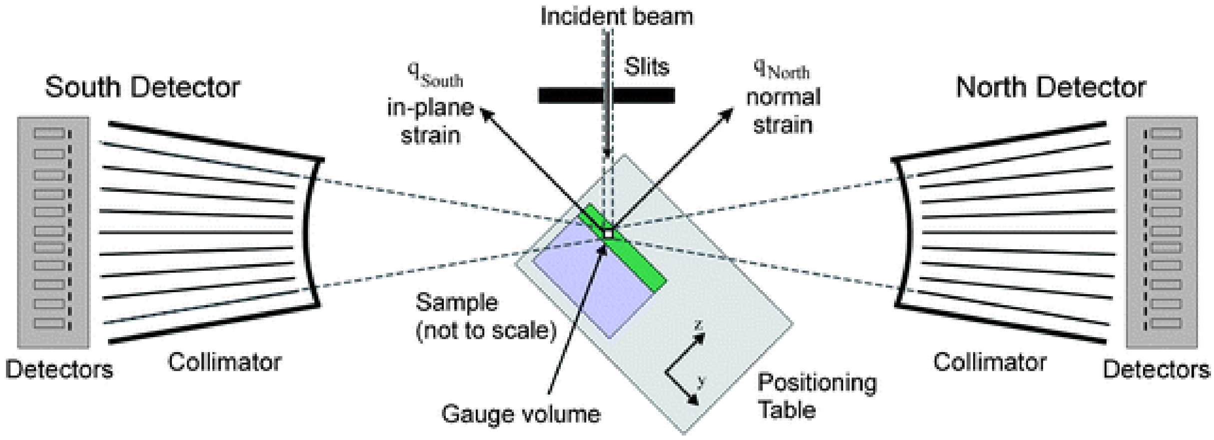

Fig. 5 Schematic aerial view of the ENGIN-X experimental setup. The volume of the sample explored by the instrument corresponds to the cuboid determined by the intersection of incident and diffracted beams, as defined by slits and radial collimators.

In this case, the collimation system of ENGIN-X was exploited for scanning the phase distribution along the thickness of a few single plates, selecting a gauge volume of 0.5*0.5*2 mm^3 (thus requiring long counting rates). Due to the strongly asymmetric positioning of the sample, however, only the North diffraction bank was used.

For the correct selection and positioning of the measurement points, the Strain Scanning Simulation Software (SScanSS) [16,17] was used. SScanSS is the ENGIN-X virtual laboratory, a very helpful tool in case of samples of complex geometry. The sample was scanned with a laser arm and a virtual model was created as input for SScanSS (see Fig. 6). The SScanSS software was then used to specify the measurement points within the virtual model of the helmet and, after the alignment on the instrument using a reference touch-probe system, the exact coordinates of the measurement points were calculated.

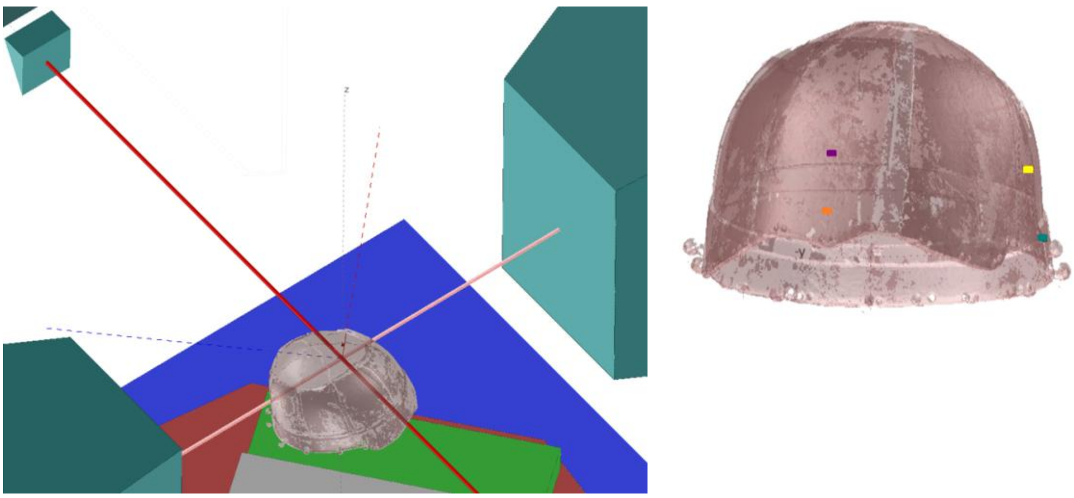

Fig. 6: (left) The ENGIN-X virtual laboratory, a three-dimensional models of the laboratory and sample used for planning the experiment. (right) Laser scanner reconstruction of the sample obtained with the SScanSS software. The position of the investigation areas is reported in different colours. The scan relative to the one in yellow is not reported because only two points out of seven were taken.

The sample was moved across the beam, along a direction perpendicular to the surface of the selected plate, in order to scan points across its thickness, collecting diffraction patterns with a step size of 0.5 mm. As the main aim of the experiment was the determination of the relative amount of the main phases (related to the intensities of the diffraction peaks), the integrated proton beam current achieved ranged 50-150 μAh, depending on the depth of the gauge volume under investigation (from the surface to the inside of the helmet respectively).

Rietveld refinement [18] was then applied to the diffraction pattern to obtain the quantitative analysis of the main phases (ferrite and cementite). The experimental diffraction data was processed through EX-SBA, the Open Genie based calculation routine for ENGIN-X [14], and then analyzed using the GSAS code [19] through the EXPGUI interface [20].

Results and discussion

An example of a refined diffraction pattern is reported in figure 7.

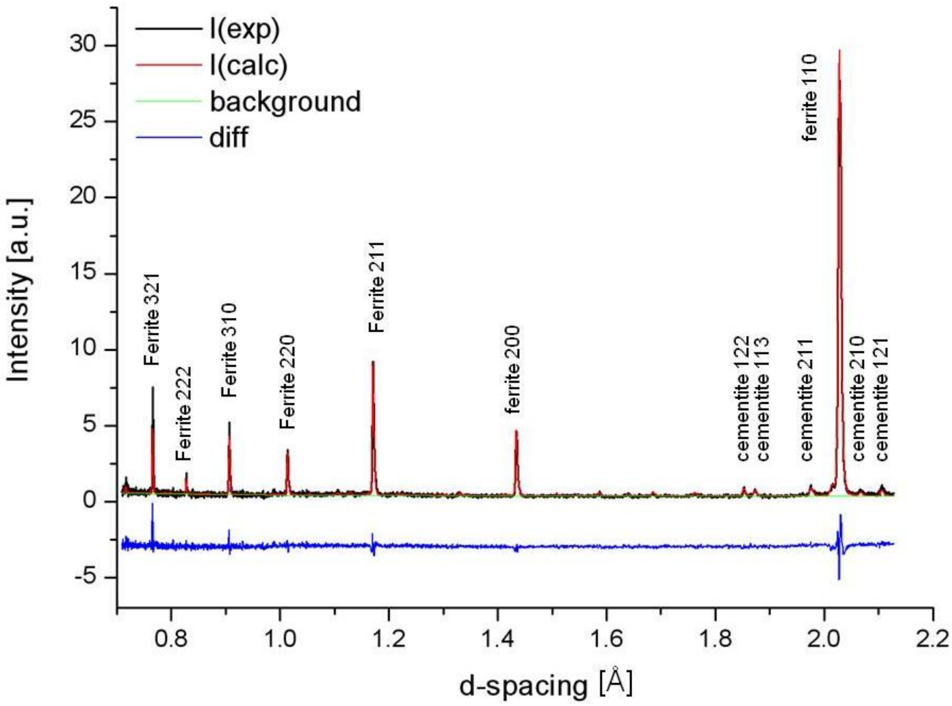

Fig. 7: Diffraction pattern relative to front plate 1 (indicated in orange in figure 6), measured at 1.75 mm depth with a proton beam current of ~80 μAh. The experimental data is represented by the black line, the calculated diffraction pattern by the red one, the difference between the two is reported in blue, and in green is the background. Only the main peaks of ferrite and cementite are labelled.

The two phases investigated are ferrite and cementite: ferrite is the room-temperature stable phase of iron, which is the main component of iron and steel artefacts; while cementite is the meta-stable intermetallic phase of iron carbide (Fe_3C) that is responsible for the hardness of steel. From the quantitative measurement of cementite, it is possible to determine the carbon content of the sample, and therefore have an idea of the properties of the steel and the technological levels achieved.

Since no measuring point contained other metallic phases (such as martensite or austenite), the conversion relationship from cementite to carbon content is simply:

$$C\,[wt\%] = 6.67\,\frac{Fe_3C\,[wt\%]}{Fe[wt\%] + Fe_3C\,[wt\%]}\,[wt\%]$$

The calculated values for each measuring point are reported in figure 8: the level of carburisation is plotted as a function of the depth of the gauge volume, from the surface of the plate through its thickness of circa 5 mm.

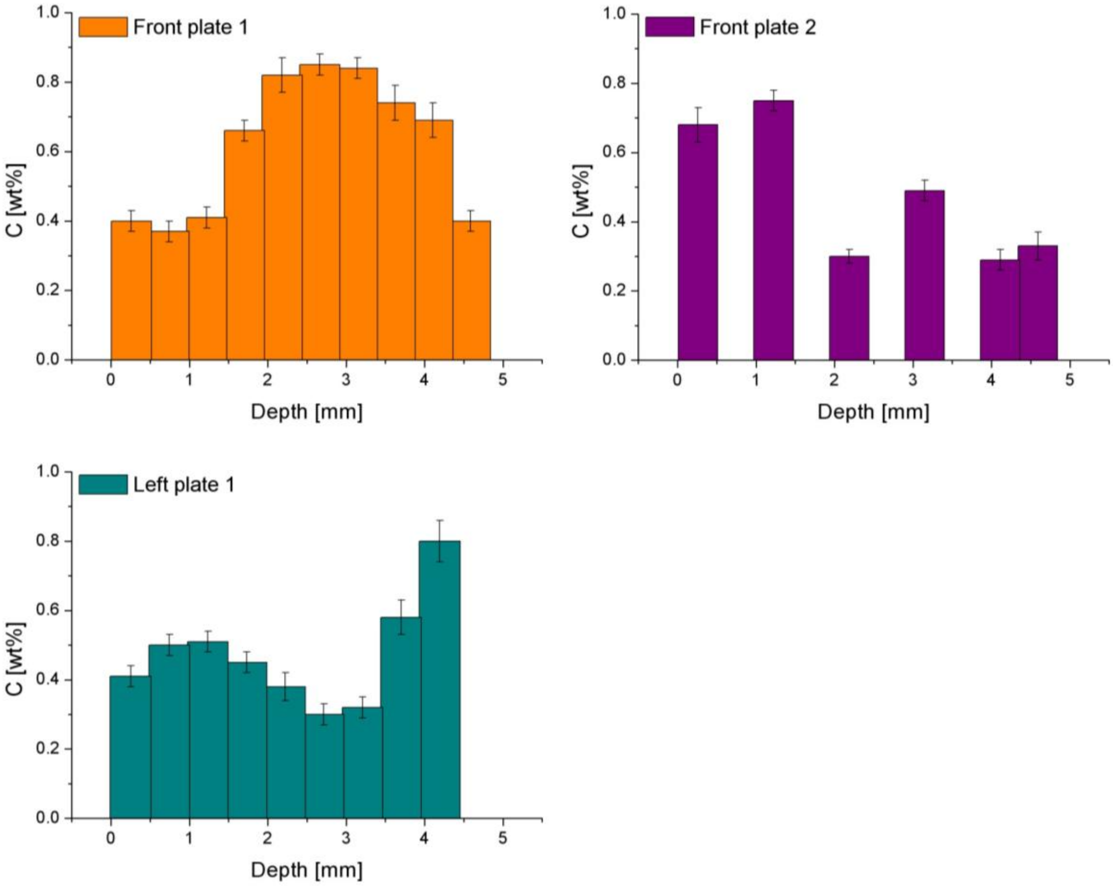

Fig. 8: Carbon content distribution from the surface of a plate through its thickness. In some cases there is an overlap in the area investigated, so that some points might be the result of areas at different carbon content. The amount of C is related to the amount of cementite (Fe_3C) normalized to the percentage of ferrite.

The overall data shows a very high carbon content in places, even higher than expected with respect to the INES diffraction results (up to ≈ 0.4 wt. % of C), where the whole thickness was probed with a spot size of 2.5x2.5 cm.

The present scans reveal the presence of a multi-layers structure that is different from the one reported in literature, at least in case of ‘Front plate 1’ and ‘Left plate 1’. Front plate 1 shows very clearly a core of high carbon steel embedded between two layers of lower carbon steel. Considering the thickness of the layers, 1.5 and 0.5 mm on the outside and inside edge respectively, it is very unlikely that the carbon content of these layers was lowered through selective oxidation since the amount is constant and then its distribution cannot be ascribed to a diffusive process.. Left plate 1 seems to have been created from only two layers of steel, with the highest percentage of carbon on the inside distributed on a thinner layer of circa 1 mm. It is also possible that a plate of banded steel was used [21], that had not been sufficiently homogenised. This latter option would explain the difference in the structure between ‘Front plate 1’ and ‘Left plate 1’.

Only front plate 2 seems to correspond to the structure described by K. Sakakibara, with an outer face of steel and an inner lining of low carbon steel. Unfortunately, in this case the sampling frequency is lower and it is not possible to discriminate with precision the thickness of the layers and their exact number.

Conclusions

Through this study we have been able to analyse the quantitative composition of ferrite and cementite of a Haruta *kabuto* from 1600. The helmet is characterised by large and sturdy plates, around 5 mm of thickness, that -thanks to former investigations- may have been made of a composite structure of iron and steel superimposed.

Detailed investigations have been performed on three plates, measuring the differences in carbon content through the thickness, performing one scan per plate.

The data obtained shows clearly that the helmet may have been constructed from two different carefully chosen materials, and skilfully worked to obtain a composite structure, such that it would provide the best possible level of protection for the wearer. The steel is distinctly harder and tougher which would help prevent the penetration of projectiles, whilst iron was thought to increase toughness. In fact, iron may be softer than steel, but bloomery iron (or *tatara* iron) is not tougher because it is higher in slag than bloomery steel, and so it would be more brittle [12,22].

The *kabuto* described in this paper represents a clear example of the technological change caused by the introduction of firearms in Japan in 1543 and is the result of the long period of conflicts that affected Japan till the beginning of the 17th century. Large and sturdy plates were better able to resist bullets and a composite structure of high- and low- carbon steel might have been able to provide good protection from both piercing and cutting blows.

Acknowledges

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