

A Ghost Story: Remnant Structures in Corroded Ancient Iron Objects

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ABSTRACT

The applicability of a broad spectrum of laboratory analytical methods to the study of remnant structures still observable in the corrosion products of ancient iron objects is discussed. These methods range from examination by light optical microscopy and SEM to direct microanalysis using x-ray mapping in EPMA. Samples ranging from low carbon iron to steels to cast iron have been examined and it has been found possible to observe remnant structures and infer fabrication information from the large majority of objects studied.

INTRODUCTION

A number of years ago, at the first MRS Symposium on Materials Issues in Art and Archaeology, I reported on the general aspects of the use of electron optical and x-ray analytical methods as applied to archaeometallurgy, and how this suite of experimental methods could be used together with an understanding of materials science in order to characterize metal artifacts and to provide insight into ancient fabrication methods [1]. In this present paper I would like to demonstrate the use of these methods, in a more focused way, in order to examine the structural and micro-chemical details of the prior metal structure remaining in the corrosion products of ferrous materials.

BACKGROUND

Plain carbon ferrous alloys may be classified according to their carbon content as steels, with less than about 2 weight percent carbon, or as cast irons, with carbon greater than about 2 weight percent. When steels are slow cooled from the higher temperature face-centered cubic solid phase (austenite) they undergo a reaction and transform to body-centered low carbon iron (ferrite) and iron carbide (cementite, Fe_3C). For a steel with composition at about 0.8 weight percent carbon ("1080 steel"), ferrite and cementite form cooperatively and simultaneously in the form of a lamellar structure called pearlite. For steels with lower carbon content ferrite forms first and then the balance transforms to pearlite; and for carbon contents higher than this, cementite forms first and then the balance forms pearlite. With prolonged heating the lamellar pearlite and the cementite spheroidize and thus give an indication of this type of heat treatment. If these same steels are rapidly quenched from austenite they form a new high hardness single phase structure, martensite.

Cast irons, depending on the presence of impurities such as Si, P, Mn and S, when cooled from liquid iron, may form an eutectic between austenite and graphite (producing "grey cast iron") or between austenite and cementite (producing "white cast iron"); the austenite then transforms as described above. Thus, in both cases, the microstructure of

steels and cast irons are strongly dependent upon carbon content, the presence of other impurities, and the cooling conditions.

An excellent review of the corrosion behavior of ferrous alloys, specifically directed to an archaeological context, has been written by Pourbaix [2]. Even in the simplest case of corrosion of pure iron, depending on reducing versus oxidizing electrochemical conditions, and acidic versus alkaline state (pH), iron may corrode, may be passivated or may be made immune to corrosion; and if corroded, may form hydroxides of various iron valence states, Fe_2O_3 (hematite), or Fe_3O_4 (magnetite). A variety of analytical methods exist to determine the identity of the corrosion products [3]. Corrosion of iron containing carbon is even more complex. Fontana [4] has reviewed the corrosion of steels with respect to microstructure as a variable, and demonstrated the sensitivity to corrosion conditions. Thus, single phase materials are generally corroded at lower rates than multiphase alloys, and defects such as introduced by mechanical working can provide local sites for enhanced corrosion. Cron, et al. [5] have shown that depending on corrosion conditions, for a pearlitic structure, either the ferrite, or cementite phase, or the interfacial ferrite-cementite region, may be preferentially corroded. Microstructural effects on the nature of corrosion products and corrosion rates are of considerable interest in modern context [6-8] and the results are relevant to the corrosion structures observed in ancient materials.

Remnant or 'ghost' images of the prior ferrous microstructure present in the corroded layers of metallographically prepared archaeological artifacts from Hasanlu were first clearly observed and identified by Knox [9] and then subsequently also found to be present in artifacts from other sites in Israel [10-13] by Maddin and coworkers. In first reports light optical microscopy was used; later work from this group included examination using the secondary electron imaging mode in a scanning electron microscope. Gold-coating to enhance reflectivity has also been used, but this method makes it difficult to switch back and forth between light microscopy and the SEM and to find the same area for examination.

Scott [14-16] has attempted to categorize these structures according to the degree of remaining local metallic material: *remnant* structures having complete grains or aggregates of metal surviving intact, *partial replacement* structures with the majority of the structure converted to corrosion products, and *fossil* structures where the form alone is preserved but with no surviving metal.

Work on remnant structures has also included analytical electron microscopy [17] where it has been possible to directly analyze carbo-nitride precipitates in the residual metallic ferrite in ancient steel, and to perform microanalysis using EPMA on large area samples of corrosion in a Japanese sword blade [18]; in this study it was possible to examine the microchemistry of the slag inclusions as well. Studies have also been performed on material from India [19,20].

The major questions raised for the study of these remnant structures are: with what degree of success are these structures found, and what are the most appropriate instrumental methods for examination?

RESULTS AND DISCUSSION

In terms of specimen preparation we have found that normal but careful metallographic preparation methods give good results, but delicate or friable corroded iron should be impregnated and mounted using a low viscosity epoxy mounting material. Specimens have been ground and polished using diamond paste, alumina or silica gel. The use of neutral pH buffered solutions is recommended. Examination should always commence with light microscopy, both at low and high magnification; the best lighting methods seem highly specimen specific and thus considerable time and experiment are necessary. A summary of benefits and difficulties encountered during the examination of a large number of objects is shown in table I.

Figure 1 shows a light microscope image of a section of a fully corroded iron knife from Tel Migne in Israel [21-23]. It is obvious that the corrosion conditions have changed drastically at some point in time, and the image shows the corrosion product to be dense on the left but quite friable and cracked at the right. The white pockets distributed throughout the entire cross section are residual cementite regions remaining from pearlite; they have been relatively unaffected despite the changing corrosion conditions. Estimation of the area fraction of pearlite in a formerly ferrite matrix indicates this material to be a wrought iron with about 0.4 weight percent carbon.

Table I. INSTRUMENT SELECTION CONCERNS

LIGHT OPTICAL MICROSCOPY

- **Unetched vs. Etched (R.Knox,B.Scott)-component loss upon etching**
- **Gold coating (R.Maddin)-enhances reflectivity but location difficult in SEM**
- **Magnification limits ability to resolve pearlite**

SCANNING ELECTRON MICROSCOPY

- **Etching not required**
- **Energy Dispersive X-ray analysis limits element detection**
- **Back Scatter mode contrast good for low Z slag inclusions**
- **Could sometimes get charging unless coat specimen (rust not a problem but slag inclusions are problematic)**

LOW VOLTAGE SEM

- **Higher magnification without coating to avoid charging**

ELECTRON MICROPROBE ANALYSIS

1. **Wave Dispersive detectors-improved detection limits**
 - **Wave Dispersive X-Ray Maps**
 - **Composition Histogram Imaging**

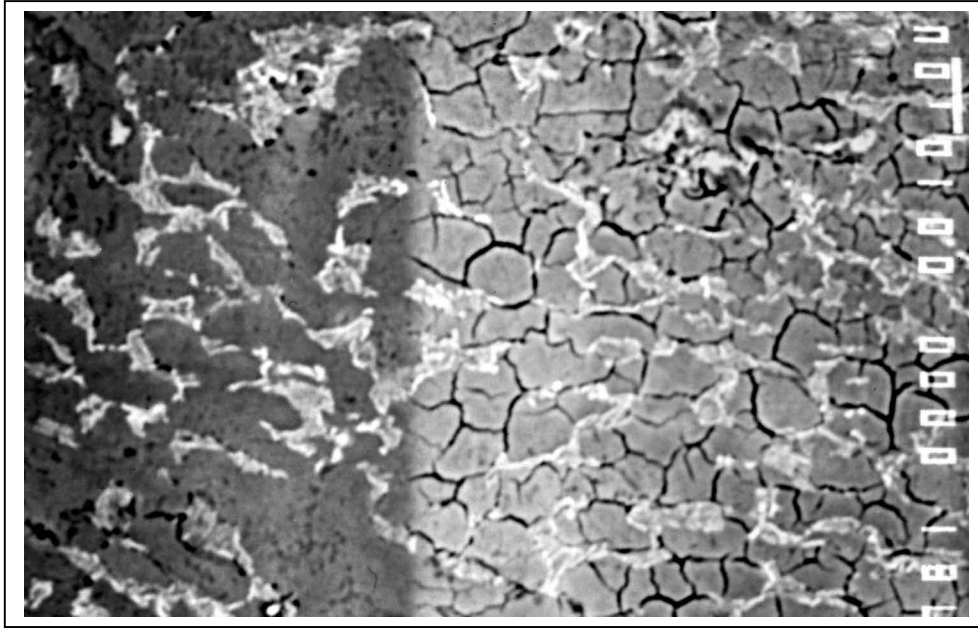


Figure 1. Metallographic cross-section of knife from Tel Mique.

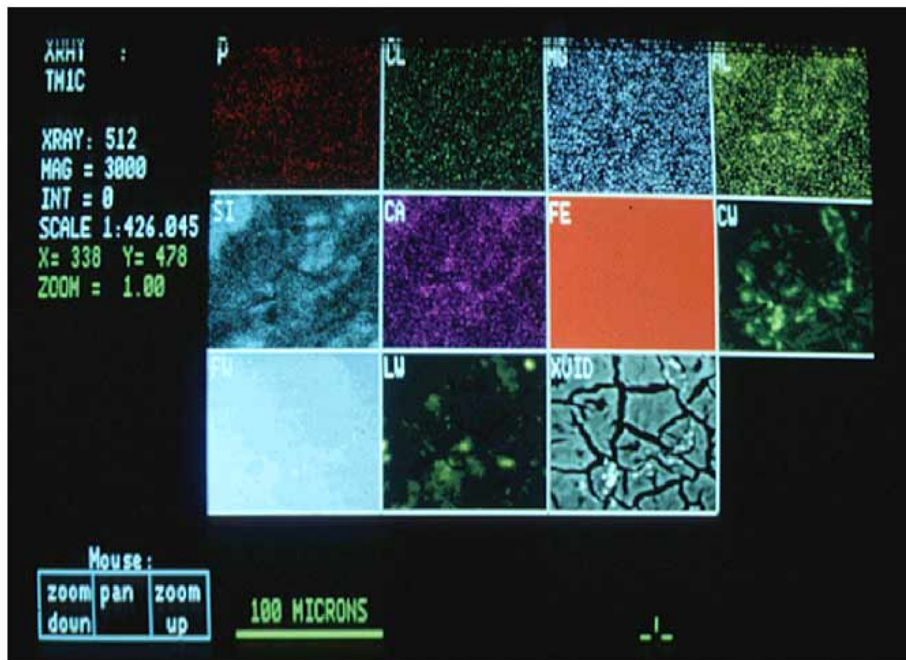


Figure 2. EPMA x-ray map of knife from Tel Mique.

Figure 2 is an x-ray map obtained during EPMA study of a small region of the knife shown in figure 1. Each box is a digital image such that different boxes are the stored x-ray counts obtained for each chosen element and at equivalent locations. The box at the right side of the lower row (marked XVID) is an electron image of the section; the box in the middle row on the right (marked CW) is a carbon map obtained using the WDS detector. Thus it is possible to perform microanalysis on the small remnant carbide contained within the corrosion product. An SEM image of another region is shown in figure 3; the bright regions are slag inclusions trapped in the corroded matrix. figure 4 is the EDS spot spectra obtained from one of these slag inclusions. The peaks for Fe, Si, Ca, P, and Cl indicate this to be a calcium iron silicate with the Cl and P probably coming from the corrosion environment.

We have obtained similar results from numerous specimens taken from knives and swords and from locations ranging from Hasanlu, to Vered Jericho in Israel, to Japan. The results obtained on the Japanese sword have been previously published [24]; in this case we used an image reconstruction method (Concentration Histogram Imaging [25]) that takes the ratio of counts for element pairs pixel-by-pixel and plots these as a two dimensional or three dimensional histogram. Certain locations in the histogram may be selected to reconstruct the image; this method can be used to locate specific compounds with specific element ratios.

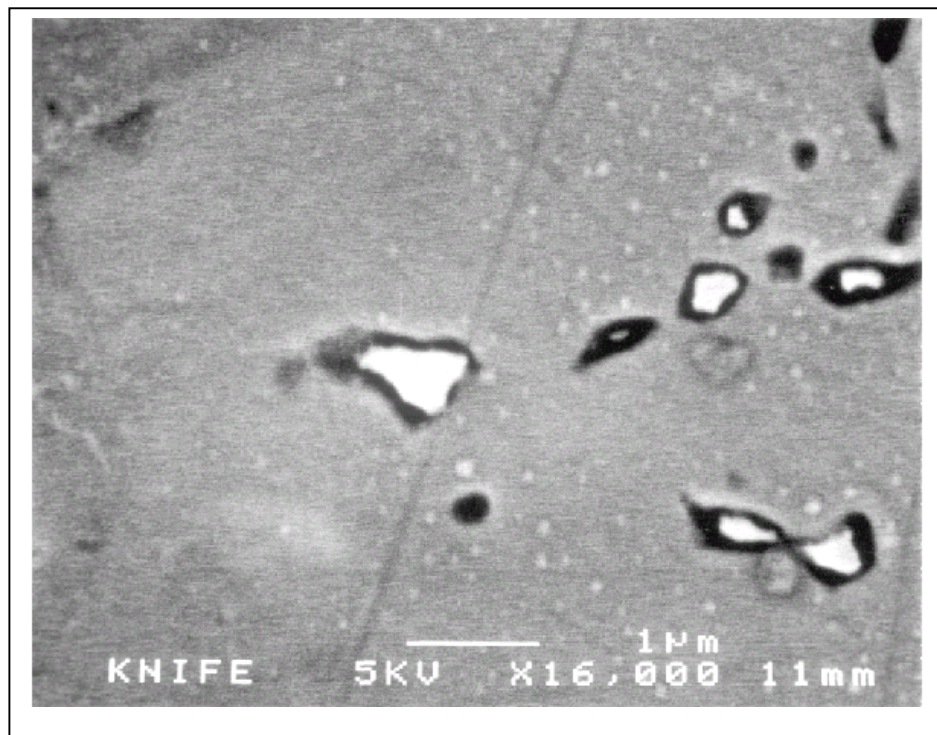


Figure 3. SEM image showing slag inclusions in knife from Tel Migne .

Cursor: 0.000keV = 0

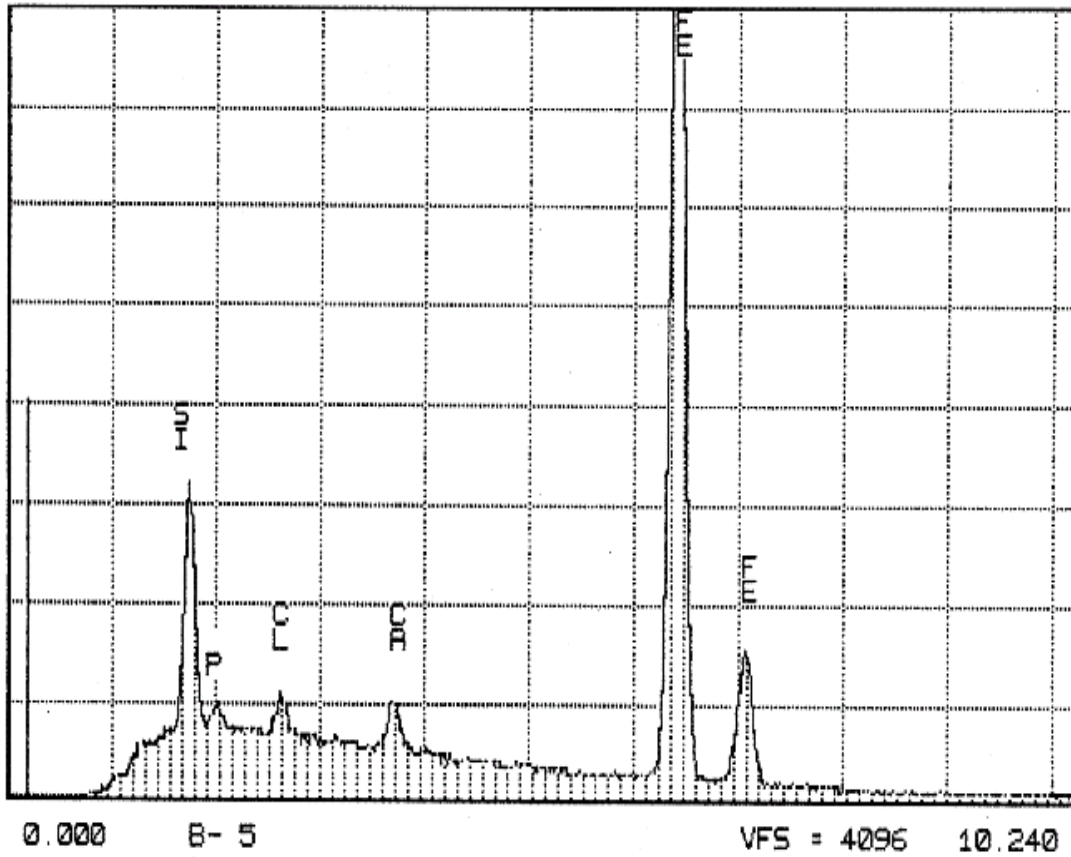


Figure 4. X-ray point spectra from slag inclusion in knife from Tel Mique.

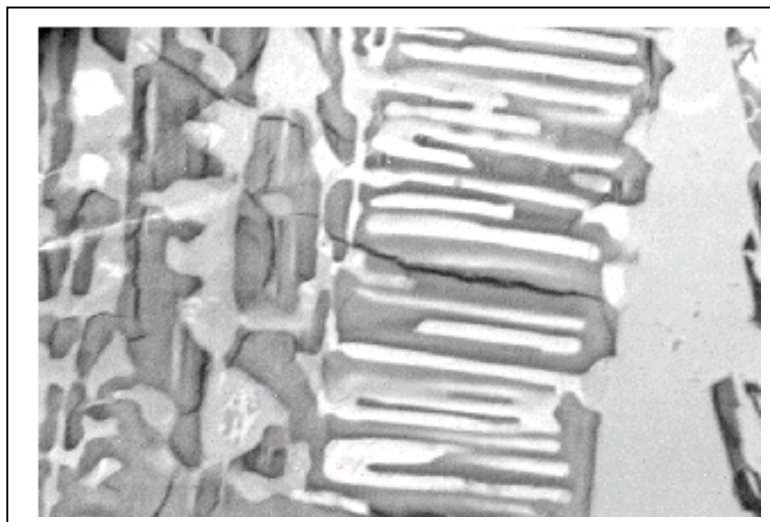


Figure 5. SEM image of ancient Chinese cast iron.

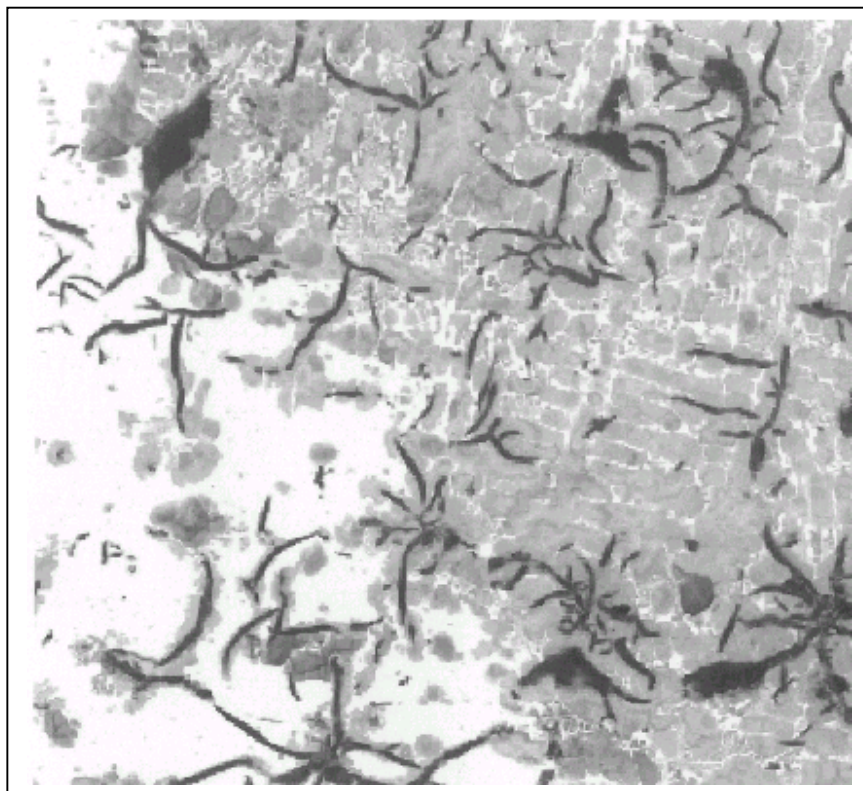


Figure 6. SEM image of Cape Horn cast iron.

Figure 5 is an SEM image obtained from the corrosion product of an ancient Chinese cast iron. The structure is interpreted to be that of a white cast iron predominantly consisting of a ledeburite eutectic. The very bright regions are uncorroded iron carbide, The EDS spectra (not shown) indicated only Fe (and C) to be present; the absence of Mn and S (usually present in later Chinese cast iron) indicates that the cast iron was produced from charcoal rather than coal. Figure 6 is an SEM image obtained from a piece of corroded iron associated with a shipwreck found on the coast at Cape Horn. The region to the lower left is the partially corroded metal matrix; the region to the upper right is the fully corroded material which has made the remnant structure more clearly seen than the metal matrix. This material is therefore identifiable as a gray cast iron.

SUMMARY AND CONCLUSIONS

It appears that remnant structures are found rather frequently in the corrosion products found on ancient iron objects, with dense corrosion sections providing samples that are easier to prepare and more likely to yield viable remnant structures. The best experimental methodology is to use an array of methods so that maximal information is gathered. The present results demonstrate that direct microchemical analysis and imaging of carbon can be obtained by EPMA equipped with low atomic number detectors. Slag inclusions may be located and identified; this means that information related to smelting and fabrication practice previously believed to be lost is in fact accessible.

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