

The effects of plasma treatment on the microstructure of metals

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ABSTRACT: *Plasma treatment became an established method for the treatment of corroding metals, particularly iron, in the 1990s. There seemed to be a general assumption that the treatment had little significant effect on the microstructure of the metals and this has never been seriously challenged. Although under the less extreme conditions now adopted in some laboratories gross phase changes may not happen, more subtle changes are very likely to be taking place, as exemplified here by a series of test pieces of iron and silver metallographically examined before and after plasma treatment. These tests are described and some of the changes in structure that are likely to occur in metals in the temperature range 100–300°C are outlined. These changes are significant and are often the result of deliberate heat treatments during the original manufacture of the artefacts. Once they have been modified by subsequent heating much of the fabrication history will have been lost. Other structural changes occur over long periods of time and these are also vulnerable to quite modest heating, thereby compromising future authentication examinations.*

Introduction

It must seem paradoxical that having pioneered research into the use of plasma treatments in conservation (Daniels *et al* 1979) the British Museum chose not to adopt the method for the conservation of metals. This decision was based on the results of a trial application of the plasma treatment to a number of corroded iron and silver artefacts from the British Museum's collections and reported after five years when some idea of the long term stability of the treated items could be ascertained (Bradley *et al* 1997).

Since that paper, the plasma method has continued to be intensively investigated and modified, and there now seems to be a more realistic awareness of its capabilities (Arnould-Pernot *et al* 1994; Voute 1997; Schmidt-Ott 1997 and 2004; Schmidt-Ott and Boissonnas 2002). In particular, operating temperatures are now generally much lower and are more carefully monitored, but there still seems to be a general lack of awareness of the potential changes to the metallographic structures of both iron and silver artefacts that can be brought about by prolonged exposure to quite moderate heating.

In this paper, some of the problems of corroding iron

and its treatment will be briefly described and the plasma process will be summarised. The structure of metals will be outlined, emphasising their general heterogeneous and non-equilibrium nature, and how these are partly the result of quite moderate heating. The surviving structures are still vulnerable to heat treatments, even those operating at quite low temperatures. This is followed by a description of the trial plasma reduction treatments made on the iron and silver test pieces back in 1991, at the more elevated temperatures current then, and the observed structural changes presented in more detail than in Bradley *et al* (1997). The paper concludes with a more general discussion of the likely effects of plasma treatments on the structure and chemistry of both metal and corrosion.

Corroding iron and its conservation

Corroding iron antiquities have always been a problem for those wishing to preserve them (Knight 1997). Compared to the other metals of antiquity, the mechanisms of iron corrosion are complex and have been poorly understood. Corrosion of iron recovered from the soil is likely to be well advanced and difficult to control. Furthermore, the sheer quantities of corroding

iron recovered from excavations can be quite daunting. Small wonder then that some curators in the past literally abandoned the iron antiquities in their care to their fate, whilst others adopted what are now regarded as draconian measures in an attempt to control the often all too visible disintegration of the ironwork in their displays and store rooms.

The mechanisms of iron corrosion have only relatively recently begun to be understood, in particular, the part played by chlorides in the corrosion of freshly excavated iron (Turgoose 1982; Knight 1997). It is now realized that the immediate cause of corrosion and flaking of freshly excavated iron is likely to be the oxidation of the deep-seated ferrous chloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, to form akaganeite, $\beta\text{-FeO.OH}$, with the attendant release of the chloride ions to attack the remaining iron. The forming akaganeite has a larger volume than the ferrous chloride, causing flakes of iron mineral to spall off the surface as a result of this expansion beneath. The traditional and current washing treatments removed the relatively harmless surface chlorides but often did not touch the active chlorides buried in and beneath the insoluble akaganeite. Hence the dispiriting discovery of fresh outbreaks of the familiar orange-yellow akaganeite on the surface of artefacts shortly after having undergone long cycles of washing that had apparently removed the chlorides. This is not to suggest that the treatments were a waste of time, washing does produce some improvement in the resistance of the iron to re-corrosion (Keene and Orton 1985). It is, however, the removal or neutralisation of the deep-seated chlorides that remains the long term objective of iron conservation.

Treatments

In ignorance of the actual corrosion mechanisms taking place, early conservation treatments were inevitably somewhat uncertain in their success (Jakobsen 1988). One early treatment was to mechanically remove as much loose corrosion as possible, wash, heat and then impregnate with hot wax. The process was described by no less an authority on antiquities than Petrie (1888) 'The only treatment is a good soaking in water, to remove soluble salt, baking in a hot oven, and then long soaking in melted wax, which should be left in all the pores and cracks'. This treatment was quite often successful as it usually sealed the inner, active corrosion layers and prevented further oxidation and the formation of akaganeite. However, it sometimes did not provide a complete seal and there were many cases where the corrosion continued unabated but unnoticed beneath the wax until the object finally and irretrievably

fell apart. For this reason the waxing of iron artefacts was discontinued many years ago at the British Museum.

Some more extreme approaches were adopted; the mineralised layers could be removed in their entirety by chemical or electrochemical means. Having lost all their original surfaces, the remaining iron looked awful and often bore little resemblance to the original artefact. Such drastic stripping operations were discontinued relatively early on, especially for heavily corroded items, although continued with some success for more lightly corroded pieces (Pearson 1972; Lacoudren). However, the treatment did remove the chlorides and the only loss of metallographic information was that contained in the mineralised layers. The remnant metallurgical structures contained in the corrosion can however be significant, as can any mineral-preserved organic materials, etc (Scott 1989).

Another approach was hydrogen reduction performed at high temperature to reduce the iron minerals back to metal (Barker *et al* 1982). This was a drastic but pragmatic approach to the treatment of large numbers of often badly corroded ferrous items recovered from marine environments. These were usually deeply impregnated with both chlorides and sulphides and were thus unstable once out of the water; they had a tendency to disintegrate rapidly and therefore needed quick attention. The iron was placed in a furnace operating at temperatures of around 800–900°C in a current of nitrogen and hydrogen generated by the cracking of ammonia. The iron minerals were reduced back to metal and such chlorides and sulphides as were present were removed as hydrogen chloride and hydrogen sulphide.

The main objections to the method were concerns over the safety of a method involving large volumes of hydrogen at elevated temperatures as well as the almost total obliteration of the original metallographic structure of the metals. Tylecote and Black (1980) pointed out the problems, especially with iron that had been heat treated. They went on to make a list of types of artefact where such heat treated metal was likely to be encountered, and seemed to suggest that it was acceptable to treat anything else by this method. Unfortunately the reality is not that simple. For example, after her study of Iron Age files, hammers and other tools from Britain, Fell (1995) remarked that 'quenching may not be predictable to the broad category of tools but rather to the purpose of individual tools'.

Archer and Barker (1987) carried out further metallurgical studies and concluded that to reduce the iron oxides a temperature of at least 350°C was necessary, and claimed

that 'only the 100% martensite and slightly tempered structures will be affected'. This statement is at best extremely misleading. Complete major phase changes may not take place, but a host of more minor but still significant changes will certainly occur (see below).

Due to the safety concerns, the hydrogen reduction method is not practised any longer in the UK but is still apparently used on maritime iron in Denmark. However, in favour of the method it must be stressed that after a relatively short treatment time the *form* of the artefact was preserved and it was likely to be stable thereafter.

More recently attention has moved again to chemical treatments, particularly desalinisation with alkaline sulphite solutions, with some success (Rinuy and Schweizer 1981; Greiff and Bach 2000). Schmidt-Ott and Boissonnas (2002; Schmidt-Ott 2004 and see below) now use a very modified form of the plasma procedure as a pre-treatment for alkaline sulphite washings.

Plasma treatments

In the 1970s and 1980s it was proposed to treat corroded artefacts with a gas plasma, that is ionised gas molecules at very low pressure (Vepřek 1993; Vepřek *et al* 1983; Patscheider and Vepřek 1986). These lose their charge when they encounter a surface and are very reactive, reducing the mineralised surface of a metal artefact back to metal, for example. The reduction itself requires no potentially damaging mechanical treatment, is non-invasive, and deemed to be less harmful than most chemical treatments. As originally described in the 1980s and early 1990s, the method comprised three main stages, the basic plasma reduction pre-treatment, following which the loosened corrosion products were mechanically removed. This was followed by a 'passivation' or 'nitriding' stage, and the metal was then mechanically cleaned again and waxed.

Plasma reduction

In some ways the development of the plasma methods could be seen as a response to the problems posed by the dangers of the hydrogen reduction method. Put very simply, in its original form the aim of the plasma treatment was to effect the stabilisation of the object by the removal of the chlorides as hydrogen chloride and the partial reduction of the oxides back to metal with a plasma containing hydrogen at very low pressures at temperatures of around 300–400°C for several hours. It should be stated here that the temperatures were those recorded by an external mercury thermometer rather than the actual temperature of the metal under treatment and

since that time better recording systems have been devised that more accurately measure the temperature of the artefact being treated (Schmidt-Ott and Boissonnas 2002). This stage and the following passivation were performed on the British Museum test pieces in 1991 and are described in more detail below.

Passivation or 'nitriding'

The next stage in the plasma process was the passivation of the surface of the artefact by so-called 'nitriding'. Plasmas made up of varying quantities of hydrogen, methane and nitrogen were supposed to protect the metal against further attack. The only reported visible change after passivation was an increase in the darkening of the metal surfaces (see below). However there is some confusion of terminology here: in English the nitriding of iron is a very specific process used to harden the surface of the metal. For example, *The Metals Black Book* (Wayman and Bringas 1995, 37) defines nitriding as holding the iron at temperatures in the region of 500–600°C in a nitrogen-rich environment which 'results in a shallow surface layer rich in iron nitrides, with a very high hardness'.

Over the past thirty years plasma nitriding of iron has been introduced, using plasmas of hydrogen and nitrogen at temperatures of between 400–800°C (but usually well over 500°C), for many hours (Staines 1990; Hombeck and Bell 1991). As the temperatures employed by the plasma passivating process are usually below this it does not seem likely that any iron nitrides would form, especially as most of the surfaces of the iron artefacts remained oxidised and thus could not react with or dissolve the nitrogen to form nitrides. No nitrides were observed on any of the surfaces examined by us, and more significantly, no nitriding was observed by Archer and Barker (1987) in their study of iron and steel which had been held at temperatures between 250–850°C for up to 72 hours in an atmosphere of hydrogen and nitrogen. They had specifically checked this point (*ibid*, 90) as Tylecote and Black (1980) had suggested it as a possibility.

Thus, no nitriding takes place and even if it did the presence of nitrides would not passivate the surface, merely harden it. In answer to queries from us, scientists working for commercial nitriding firms suggested that sooting from the cracking of the methane in the plasma could be the cause of the observed increased blackening of the surfaces (T Staines, technical director of NRS Nitriding Services, Telford, Shropshire, pers comm). If this is so, the contamination of the surfaces with these organic materials could itself result in long term corrosion problems.

Thus, the so-called plasma passivation or nitriding phase would seem to be no more than a continuation of the reduction stage, usually carried on for much longer periods and during which more corrosion was loosened. We note that in recent descriptions of the plasma process the term nitriding is no longer used and in fact that whole stage in the process seems to have been dropped.

Waxing

The final stage in most of the treatments remains a passivation with hot wax. This was the one part of the standard process that was omitted in the treatment of the British Museum artefacts, for the reasons given above. Without this some of the British Museum treated artefacts were re-corroding within weeks of treatment (Bradley *et al* 1997), and many more were corroding after five years. This does suggest that the waxing is a significant part of the overall process in inhibiting corrosion, something that Petrie seems to have been aware of back in 1888.

As already noted, the trend through the last ten years at the major institutions researching and using plasma treatments has been for operating temperatures to become lower. Arnould-Pernot *et al* (1994) were still recommending temperatures of between 300–350°C for several days as the single treatment, but more recently Schmidt-Ott and Boissonnas (2002) at the Swiss National Museum have used plasma treatment

at around 120°C, or even lower (Schmidt-Ott 2004), to loosen the corrosion on iron artefacts prior to standard sodium sulphite treatment. However the low level heat treatments are by no means universal, and even where they are followed the potential risks to the microstructure are still not fully enough appreciated (see below).

Effects of heat on metallographic structures

Iron and steel

The microstructures of metals are often complex and heterogeneous, the result of the heating and working of the metal (Figs 2–4). Indeed, the microstructure might be thought of as a page on which the object's technological history has been written.

The changes in structure of iron-carbon alloys across a wide range of compositions and temperatures under equilibrium conditions are published as the familiar phase or equilibrium diagrams (Fig 1). Unfortunately equilibrium conditions are often not attained, so the metallographic structure is not as predictable as the diagrams would suggest. In reality many of the transitions are quite slow so unless the cooling period is immensely long, will not have been completed, or in some cases barely begun, in antiquities after the passage of millennia. Sometimes the craftsmen held items at elevated temperatures for long periods (known as soaking) specifically to make sure that transitions had gone to completion. Conversely, the transformations may be very quick, and if an intermediate structure is desired very rapid cooling (quenching) can be used

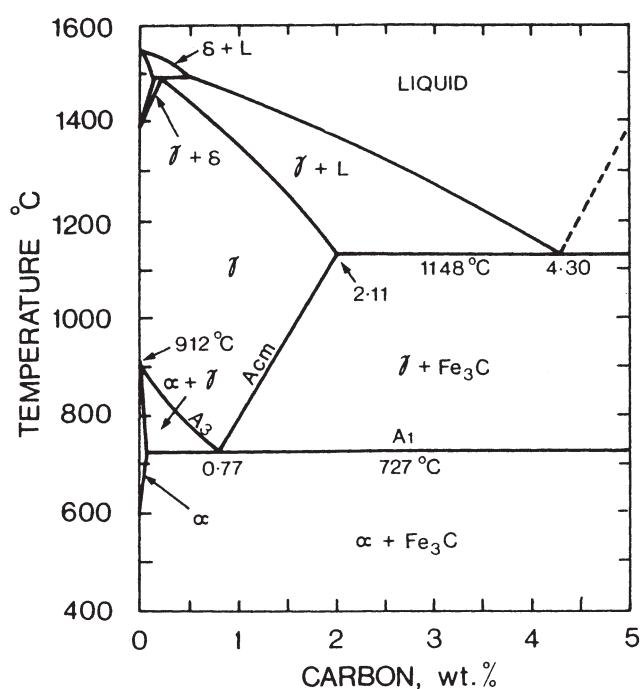


Figure 1: Phase diagram for iron-carbon (from Samuels 1980)

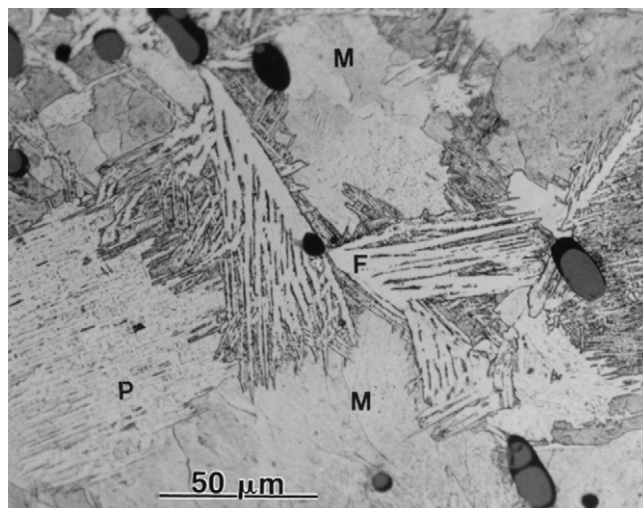


Figure 2: Micrograph of Iron Age hammer head 4 from Bredon Hill (Fell 1993), showing typical complex bainite structure of acicular ferrite (F) intersecting ferrite plates (P) and irresolvable matrix (M). This was a central part of the section cut from the hammer head where the cooling was slower allowing the bainite to form; etched with nital and bisuphite (V Fell/English Heritage).

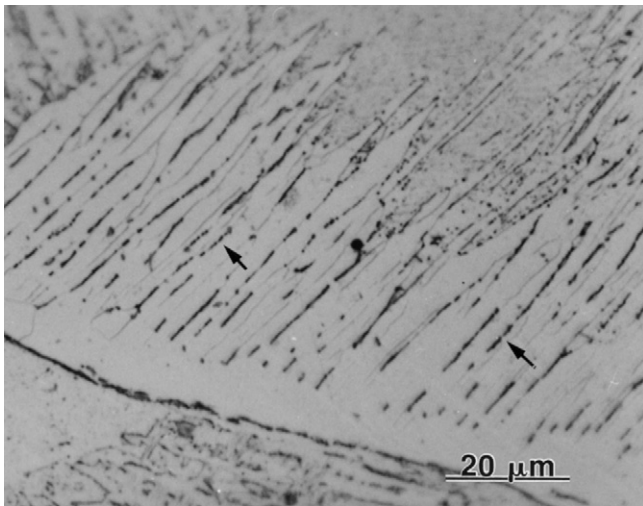


Figure 3: Detail of the bainite region of Figure 2, showing the acicular ferrite plates (running from lower left to top right) with aligned particles of carbon or carbide (V Fell/English Heritage).

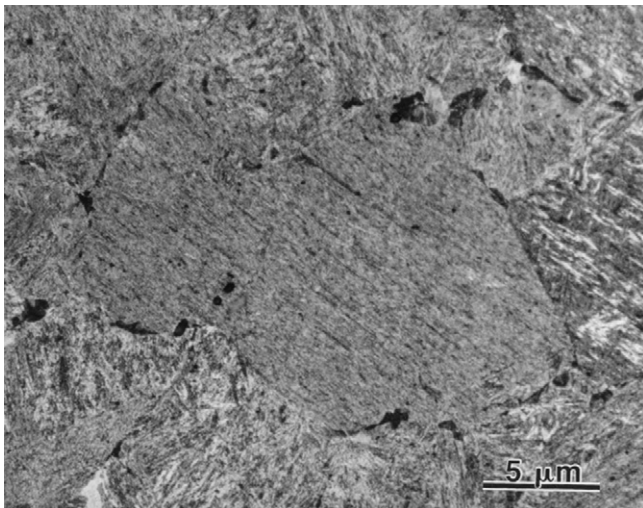


Figure 4: Micrograph of Iron Age hammer head 2 from Bredon Hill (Fell 1993), showing detail of the martensite (with traces of grain-boundary nodular pearlite). The degraded appearance of the martensite is typical of tempering after quenching; etched with nital, the dark etching is characteristic of a tempered structure (V Fell/English Heritage).

to ‘freeze’ the structure so there is no time for the equilibrium structure to form. The resulting structure can be a useful guide to the cooling rates. These can often differ quite significantly over various parts of even quite small and simple shapes, mainly depending on the thickness. Thus the structure is very often a frozen record of the metal in a dynamic state during the final stages of metalworking.

When iron is heated to above 727°C any carbon present will form a solid solution with the iron (Fig 1). This phase is known as austenite. If the metal cools down very

slowly the austenite will all transform back into almost pure iron (the phase known as ferrite), and the excess carbon reacts with some iron to form the compound iron carbide (Fe_3C), known as cementite. Thin layers of ferrite and cementite alternate to form a structure known as pearlite. These phases are stable at ambient temperatures. The actual structure and arrangement of the ferrite and pearlite depend on the rate of cooling and on subsequent reheating.

If the metal is cooled very quickly from above 700°C to ambient temperature by plunging into water, there is not enough time for the transformation described above to take place, and instead a new metastable phase known as martensite is formed by a slight change in the dimensions of the crystallographic lattice which allows more carbon to be accommodated at lower temperatures. The martensite transformation generates vast numbers of structural dislocations on a microscopic scale and consequently the metal is very hard but also brittle. Austenite does not always transform completely to martensite. If the metal is quickly cooled to below 450–500°C and then less rapidly, there may well be chance for another phase to form, known as bainite (Figs 2–3).

Because of the rapidity of the heat treatments used, the temperatures vary across the object. For example, the thin exposed edge of a blade would cool much more rapidly than the protected interior of the central rib and between the two there would be a temperature gradient, recorded by the changes in the structure of the metal. In the medieval period, and earlier, phenomena such as this were deliberately manipulated to give the required structure (Williams 2003, 898–900) and may in fact be the precursor of tempering. In the process known as slack quenching a substantial object, often of steel, or what the craftsman hoped was steel, was given a quick quench, then withdrawn and the heat retained in the core of the metal could temper the quenched steel at the extremities which would have cooled very quickly and as a consequence would be much harder. A good example is provided by the study of some iron and steel tools from the great Celtic *oppidum* at Manching in Bavaria (Schwab 2002). The quenched martensite structure at the edge of a blade had been tempered by residual heat from the core of the blade, thereby preserving a record of the interrupted heat treatment process actually taking place. So, often the preserved metallographic structure is the product of a dynamic non-equilibrium state, frozen as the metal cooled, and as such is a record of their heat treatment.

The quenched metal may be made less brittle by the pro-

cess known as tempering. That is, after quenching, the metal is carefully reheated to temperatures of between 150–300°C, depending on the degree of relief required to reduce some of the stress in the martensite, and thus some of the hardness (Fig 4). The temperatures, and thus the degree of tempering, are indicated by surface colour changes, progressing from yellows and browns (*c*200–250°C) for punches and drills to purples and blues (*c*270–300°C) for cold chisels and wood saws. Industrial processes temper batches of material for approximately an hour, but it is possible to temper a small item such as a knife blade or chisel in just a few minutes. Although not strictly a tempering process, some of the strain in quenched steel can be relieved by placing it in boiling water, making the metal less susceptible to cracking (Allen 1969, 178–9). The changes are not observable in the metallographic structure by light microscopy or SEM, but there is a fall in the hardness and in the response to etching, showing that real changes have taken place. As Tylecote and Black (1980) stated ‘We know that its [martensite’s] stability breaks down at temperatures approach 100°C, but most changes are very sensitive to temperature rather than time and a temperature not exceeding 60°C for 2000 years is probably quite capable of preserving martensite in its original form, whereas a temperature of 100°C for 1 hour would be capable of changing it ...’ before concluding ‘... once we permit thermal conservation treatments which approach 100°C we shall never know just what was the original heat treatment given by the smith, and another important chapter of our metallurgical history will be lost’.

The effects of heating at the relatively modest temperatures now associated with the plasma process are not likely to cause major transitions, such as totally changing one phase into another, but even modest heat can cause significant changes in hardness and in grain structure, such as the blurring of the local heterogeneities that were indicative of interrupted transitions etc. The evidence of any original heat treatment that had been carried out at or below the temperature of the plasma treatment will have been obliterated and, more seriously, on a treated artefact it will be impossible to know whether the observed fine detail of a structure is due to heating during the original working or more recent treatment. It will also make an assessment of the extent of final cold working more difficult.

There is the danger that once a steel artefact has undergone plasma treatment it will not be possible to determine whether it had originally been tempered. As tempering indicates a certain degree of technological sophistication, the loss of this information cannot be

dismissed as unimportant. In her study of Iron Age hammers from Britain, Fell (1993) noted that some had been tempered after quenching (Fig 4). Her (1995) study of the broadly contemporary files showed that some had been quenched and some had been air cooled, but conversely none had been tempered. This recalls one of Vepřek’s case studies, where an anonymous length of iron that had lain on a museum shelf for many a year under a thick corrosion layer had the layer removed by the plasma process, revealing a fine file (Vepřek 1993, 81). The plasma process had operated at 350°C so the file is now thoroughly tempered; whether it was originally so can now never be known.

It is certain that many structural features are not yet being detected by visual means. This is made clear by hardness measurements. Although the hardness of a metal is directly related to its structure, it is a common experience that heat treatments often result in significant and permanent changes in hardness, but without an observable change in structure. This is an important point and should be considered when it is claimed that proposed heat treatments produce no structural changes, though altered hardness values show that changes in structure must have occurred.

In common with other analytical and examination techniques, metallography has progressed enormously in the recent past; in the scanning electron microscope for example. As a result, previously invisible nuances of structure can now be observed and recorded and it is to be expected that these improvements will continue. Continuing research on the metallography of iron artefacts with improved equipment is revealing evidence of hitherto unnoted treatments. A good recent example is provided by the work of Swiss and McDonnell (2003). They noted that some low-carbon iron artefacts have unexpectedly high hardness values. This can sometimes be identified as the result of cold work but when, as here, there were no distorted grains visible, another explanation must be sought. One suggestion, in the absence of any hardening elements such as phosphorus, might be that the iron had been subjected to a solution heat treatment. This involves cooling to below 700°C, quenching in water and then ageing for two days at 50°C. By this means carbon is retained in the super-saturated ferritic material. Such a heat treatment would result in a hardness value of *c*180 Hv (Vickers hardness). This is almost twice what might be expected for apparently annealed or unworked iron with 0.03%C but the hardness would be reduced to less than 100 Hv by holding for only five minutes at 300°C (Samuels 1980, 106–7). This preserved but ephemeral evidence of sophisticated

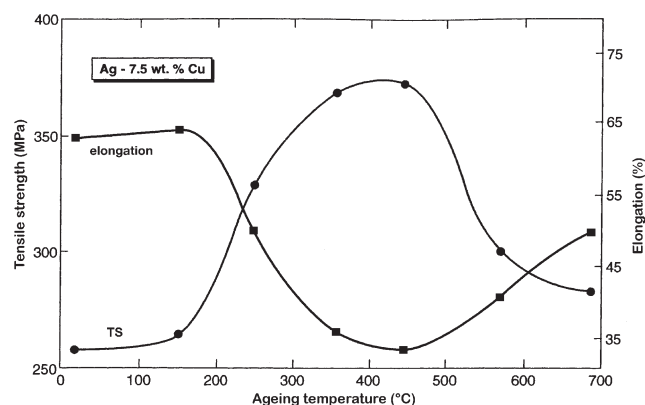


Figure 5: Changes in the mechanical properties of silver due to the precipitation of copper from the silver alloy brought about by 30 min heating (after Norbury 1928).

processes could be put at risk by plasma treatments even at low temperatures.

Silver

A major potential problem with the use of plasma treatments on silver alloys is the precipitation of copper from the alloy at the grain boundaries at elevated temperatures. In equilibrium conditions at ambient temperatures copper has a very low solubility in silver (about 0.1%). However, in practice at ambient temperatures the copper is only shed very slowly from the alloy, and in most silver artefacts of all periods the majority of the copper remains in solution. If the silver is gently heated the copper begins to precipitate at the grain boundaries, above about 150°C the precipitation is accelerated, and in the region of 200–500°C should proceed rapidly (Fig 5, after Norbury 1928; Cohen 1937). Some precipitation is likely to have occurred during the original fabrication of the artefact, either as a casting cooled down, or if the piece was hammered whilst hot, or annealed after cold working. Thus, as with the iron, changes in the structure which were proceeding rapidly at elevated temperature will have been interrupted and stopped as the metal cooled. The metal would be left with the structure in an arrested condition, arrested that is, until the next time that heat was applied.

The precipitated copper sometimes forms distinctive lamellae at the grain boundaries which are observable on some silver antiquities that have been buried for many centuries. The preferential corrosion of these copper-rich bands is probably one of the main causes of the observed distortion and embrittlement that is sometimes observed in silver antiquities (Thompson and Chatterjee 1952–4; Smith 1967; Werner 1967; Wanhill *et al* 1998; Wanhill 2003). Schweizer and Meyers (1979) suggested that it was possible to differentiate between the very slow

precipitation that had taken place at ambient temperatures over centuries, if not millennia, and the more rapid precipitation at elevated temperatures. The precipitated lamellae were found to be more widely spaced in the latter case, and thus it was argued that the recognition of the finely spaced lamellae could form a method for the authentication of silver.

Thus, to some extent, the degree of precipitation is a record of the fabrication process and, where it occurs, the form of the precipitation can demonstrate that the silver is likely to be of considerable age; the phenomenon has never been observed on British ‘antique’ silver of post-medieval date, for example. All of this information is likely to be at risk in any treatment carried out at temperatures above about 150°C.

Previous comments on the likely effects of plasma treatment on metallographic structures

In the literature on plasma treatments there seems to have been an unfortunate and simplistic assumption that steel with a martensitic structure is the only metal likely to be adversely affected by the plasma treatment, and that providing the plasma treatment does not completely obliterate this, no information has been lost. It has been claimed that the standard plasma reduction method operating at temperatures in the region of 150°C does not affect the metallographic structure of iron and steel. To metallurgists this has always seemed inherently unlikely, especially as some of the standard heat treatments during manufacture are routinely performed at temperatures of 150–300°C before being given a final treatment in boiling water.

Havlinová *et al* (1998) for example stated that ‘Only quenched steel could change its metallographic structure during plasma treatment (with a high temperature and over a long period)’. They continue ‘... the content of carbon was very low (0.05–0.15%) and therefore these swords were not quenched’. Thus they felt confident that as the iron antiquities they were treating had low carbon contents there could be no change to the metallographic structure, and that the swords could not have been quenched. In fact it is quite likely that quenching operations may have been attempted on the swords, resulting in changes to the structure and hardness of the metal even though martensite had not formed. Alternatively, they may have been cold-worked. Evidence of these and other treatments on forged iron, such as annealing, would be detectable until such time as another heat treatment was applied.

In their recent review of plasma treatment Schmidt-Ott and Boissonnas (2002) address the problem of the changes to the metallographic structure liable to result from the plasma treatment, but confine their attention to martensite. They quote from others' experiments. Ehrenreich and Strahan (1987) examined the structure and determined the hardness of tempered and untempered quenched steel discs after boiling in water. The steel disc that had been quenched and then tempered at 250°C was unaltered by treatment at 100°C, as one might expect, but the untempered quenched steel disk was significantly softened by these low temperature treatments. This is hardly surprising or indeed even new, as it is standard practice to temper as-quenched martensitic steel in boiling water. Schmidt-Ott and Boissonnas (2002) interpret the experiments as showing 'that boiling of quenched steel artefacts around 100°C will not substantially bias archaeometallurgical studies, since both grain structure and hardness should remain characteristic of martensite'. What was actually found was that although the previously untempered structure still contained martensite, it *had* been modified. In fact the difference in response to etching metallographic samples with nital (very slow in the case of untempered martensite and very fast after tempering) shows clearly that a significant change has taken place within the martensite during tempering, and the hardness values would have been modified.

Schmidt-Ott and Boissonnas (*ibid*) continued, selectively quoting from the results of Archer and Baker who, they say, 'mention that temperatures of up to 250°C as still being suitable temperatures for treatment of corroded iron artefacts'. However, Archer and Barker (1987), actually found that there was a drop in hardness from 872 to 576 (measured on the Knoop hardness scale) for

the quenched steel specimen after treatment and there was 'no trace of original martensite structure'. Even for the tempered steel specimen the hardness had dropped from 599 to 565.

Finally, Schmidt-Ott and Boissonnas (2002) quote from Perlik (2004), who 'observed the first changes in martensitic structures around 250°C'. This flies in the face of common metallurgical experience as Samuels (1980, 386–7), the standard technical reference on the metallography of steels, shows the structural changes which take place in a modern steel containing 0.4%C between 200–300°C, including a marked increase in response to etching with nital and a corresponding drop in hardness from 630 to 540 HV. Another standard text, *The Metals Black Book*, states that 'tempering even at relatively low temperatures (*eg* hours at temperatures as low as 150°C or 300°F) then the amount of carbon diffusion can be sufficient to permit important changes in the martensite' (Wayman and Bringas 1995, 23; Fig 6). Thus, the situation with most archaeological iron is likely to be very different from that envisaged by Schmidt-Ott and Boissonnas with their over-emphasis on the preservation of evidence of martensite.

Plasma reduction of British Museum artefacts

If the claims being made for plasma reduction back in the 1980s and early 1990s were correct then the method would have been the solution to some of the major problems facing metals conservation. After treatment the artefacts that had been waxed certainly looked impressive, but what was their long term stability and what changes had taken place beneath the cosmetically treated surfaces? What, if anything, had happened to the corrosion layers and what changes had occurred in the original metallographic structure of the metals?

In 1991 the British Museum carried out an investigation on 22 iron and 3 silver artefacts in various stages of corrosion and stability which were selected from their collections. Christian Eckmann of the Römisch-Germanisch Zentralmuseum Mainz, who was very experienced in the operation of plasma treatments, kindly agreed to carry out the work in conjunction with two metals conservators from the British Museum using the plasma apparatus established by Stanislav Vepřek at the Institut für Chemie der Informationsaufzeichnung der Technischen Universität at Munich.

The reduction and passivation plasma stages and the mechanical cleaning were carried out, but the waxing was omitted although some pieces were coated with the

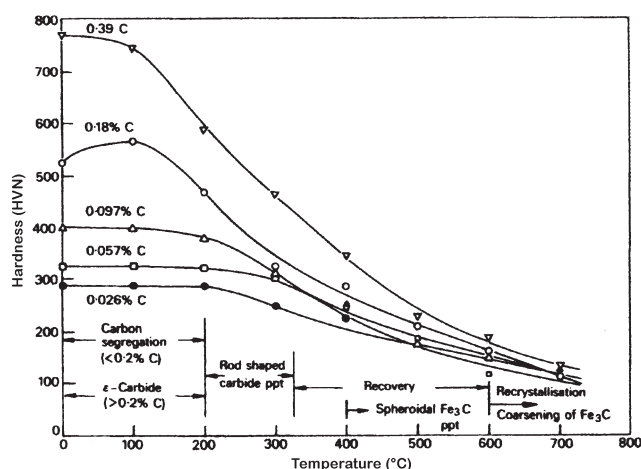


Figure 6: Hardness of iron-carbon martensites tempered for an hour at 100–700°C (from Speich 1969).

Table 1: Iron artefacts examined by metallography with summary of structures visible (from Bradley *et al* 1997).

Sample no (BM Acc no)	Inclusions	Etched structure	Changes after plasma
935 Iron Strip (1882,2-6,27)	Many inclusions, some 2-phased, all over the specimen, wide variety of size and shapes. Small and elongated near surface.	Mainly ferritic with one area of ferrite and pearlite near the surface. Traces of cold work near surface. Disturbed grain boundaries due to impurities. Precipitated carbides in grains and boundaries near C-richer surface.	Traces of working at the surface removed. Increase in disturbance at grain boundaries in metal.
938 Knife (OA5691)	Few small elongated inclusions, mainly found parallel to the surface.	Banded structure of irresolvable pearlite and ferrite with some proeutectoid ferrite.	Pearlite now resolvable. Appearance of some disturbance in the grain boundaries.
939 Lynch pin (GW/JK/JN)	No metal remains in the 'before' section. The 'after' section has a moderate number of medium to large 2-phased inclusions generally distributed, some elongated, otherwise irregularly shaped.	Large grained ferrite with fine precipitate of carbides at the grain boundaries; disturbed grain boundaries.	No indication of the original structure.
940 Coulter (ML5640)	A few small elongated inclusions.	Probably 3 layers, parallel to surface; ferrite with carbide at grain boundaries; ferrite and pearlite; same, with some distortion and possibly decarburisation near the surface.	Not much change visible.
945 Lynch pin (1892,11-4,4)	Moderate number of irregular 2-phased inclusions.	Mainly ferritic structure with some ferrite and pearlite at one surface. Carbides in grain boundaries.	Banding more noticeable, grain growth and carbides. Disturbed grain boundaries appear.
946 Sickie (1882,1-3,269)	Moderate number of small inclusions in bands parallel to the surface.	Variable carbon content with Widmanstatten structure at one surface, grain size small, some grain boundary distortion.	The grain size is increased, with more carbide precipitated.

acrylic polymer lacquer, *paraloid B72* (Bradley *et al* 1997 and below). The application of the lacquer is standard practice on metal artefacts in the British Museum, and allowed a more objective assessment of the longer term effects of the plasma treatment to be made when compared to artefacts which had not undergone plasma treatment. Prior to treatment the selected artefacts were carefully described, radiographed, photographed and selective scientific examination carried out (Table 1). Samples of the corrosion products were taken from six of the iron artefacts and two of the silver pieces and identified by X-ray diffraction (XRD). Sections were cut for metallographic examination from six ferrous and two silver items prior to treatment and from adjacent to the original section after the treatment to provide a comparison.

For the reduction stage plasmas made up of $H_2 : CH_4$ at pressures of 100–120 : 60–70 torr were used at temperatures of 250°, 260° and 270°C for periods of 2.5 or 4 hours. The loose corrosion was then mechanically removed and 17 of the iron objects were selected for the passivation treatment. For this the operating parameters were as follows: plasma made up of $H_2 : CH_4 : N_2$ at pressures of 50 : 20 : 110–130 torr, at 270°C for periods

of 12–13.75 hours. Three objects were submitted to a second passivation treatment for a further 15 hours. The passivation treatment rendered the surfaces of the artefacts a uniform grey colour.

At the conclusion of the treatment the objects were reported to be stable and, without the usual waxing treatment, were returned to the Museum for further study and observation. Visual changes in the colour and loss of information such as evidence of wood preserved in the minerals of the corrosion were recorded. XRD carried out on the iron items two weeks after they had returned showed that in general the hematite had been reduced to magnetite, but more significantly, akaganeite was identified on two of the objects. The pieces selected for metallographic examination were resampled and then all of the treated pieces were returned to the Museum's storage. It was observed that after only a couple of months several of the pieces had active corrosion, with akaganeite identified in the orange spots forming on the surfaces. After five years the group as a whole was judged to be in no better condition than the remainder of the comparable British Museum iron stored in similar conditions. The treated silver artefacts remained stable, similar to comparable untreated artefacts.

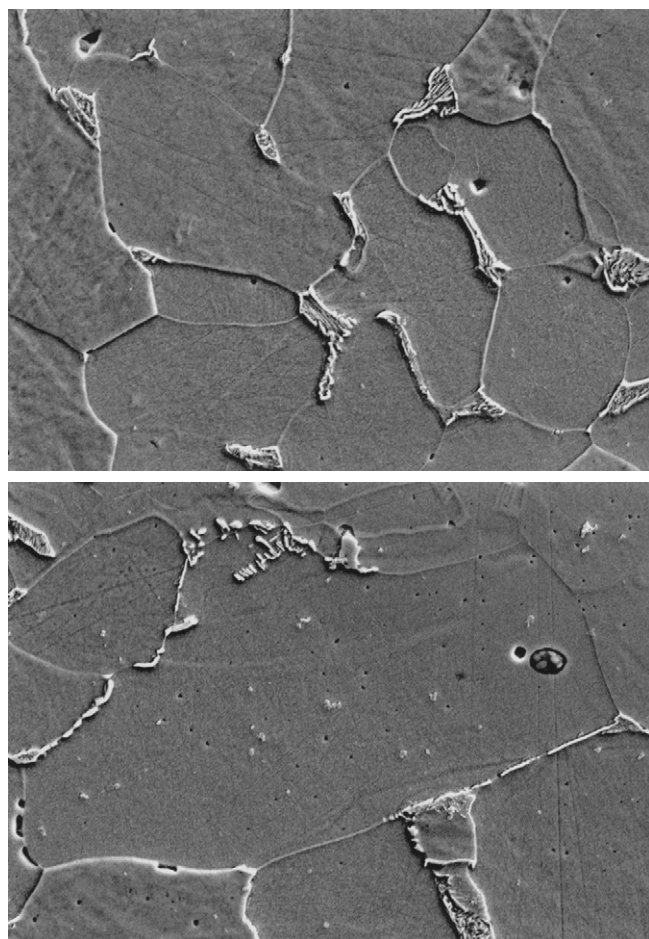


Figure 7: SEM micrographs of the structure of linch pin 945 (x350). Above: before treatment, below: after treatment. Note the grain size has increased, the pearlite has become much more distinct and the carbides have precipitated at the grain boundaries.

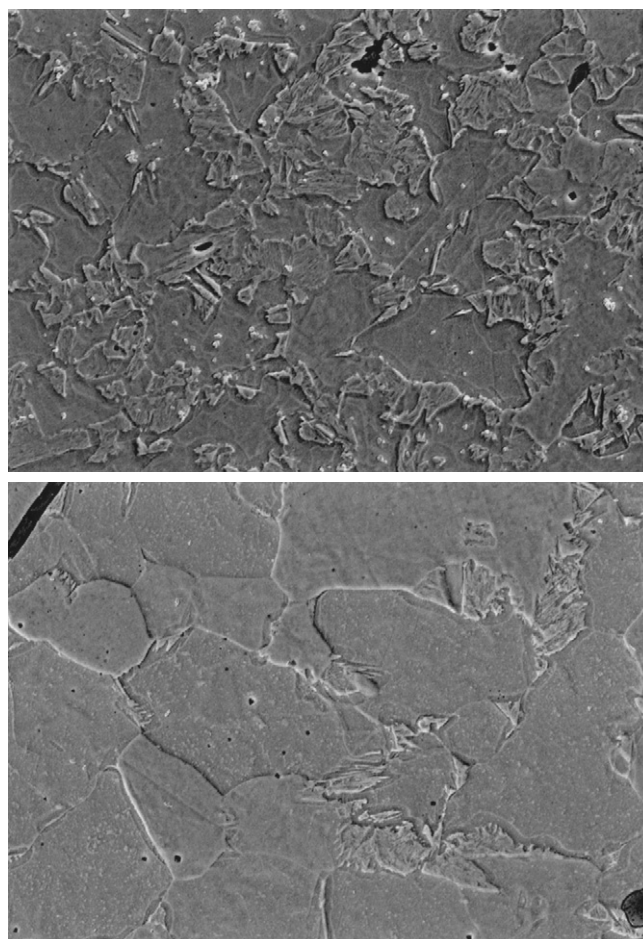


Figure 8: SEM micrographs of the structure of knife 938 (x350). Above: before treatment, below: after treatment. Note the grain size has enlarged, there is some precipitation within the grains and some of the pearlite has become more resolvable.

Metallographic examination of the plasma-treated artefacts from the British Museum

Iron

Metallographic sections were cut from a knife blade, a coulter and a sickle blade, where some heat-treated steel could be anticipated, as well as two linch pins and an iron strip (Table 1). However, there were practical problems because some of the objects were not of a uniform shape and there were also marked differences in the penetration of corrosion over very short distances that sometimes made direct comparison between the 'before' and 'after' sections very difficult. Both sections were mounted in the same block of araldite for ease of comparison.

The polished sections were examined by scanning electron microscopy (SEM), after coating with carbon to prevent charging in the electron beam (Figs 7–8). Energy dispersive microanalysis (EDX) within the SEM was used to analyse the body metal and to identify some of the inclusions. EDX was also used to prepare distribution

maps of elements such as sulphur and of chlorine penetrating into the metal along grain boundaries and through the corrosion (Fig 9, Table 3). Afterwards the sections were re-polished, etched with nital, and examined with an optical microscope and their hardness determined with a Vickers micro-hardness tester (Table 2).

None of the artefacts selected had a martensitic structure; moreover, the carbon content of samples 935, 939 and 945 would have been too low for any martensite to have formed, no matter what heat treatments had been applied. Thus according to some of the claims made previously, plasma treatment should have caused no change to the structure. In fact the structure of all the iron artefacts was changed by the treatments as evidenced by both their appearance (Figs 7–8, Table 1) and the hardness of those tested (Table 2). On sample 935 evidence of surface working was preserved in the mineralised layers, but after treatment these layers had disappeared. On three of the artefacts (samples 938, 945 and 946) grain growth had taken place during the treatment, and

Table 2: Hardness measurements before and after plasma treatment (Vickers diamond pyramid, 100gf) (adapted from Bradley et al 1997).

Sample	structure	Hardness (VPN, 100gf)	
		before	after
938 knife	—	221*	176*
939 lynch pin	carbide ferrite	210* 150*	228 156
946 sickle	C-rich	190*	181*
	low C impurities	189	165
	ferrite impurities	200	206

Notes: * = average of 4 readings, + = average of 3 readings

this was also indicated by the deposition of carbides at the grain boundaries. Impurities such as phosphorus and oxygen, dissolved in the body metal of samples 939, 945 and 946, had developed poorly-defined, but none the less real, substructures within the grains and around the grain boundaries during the treatment.

Changes due to heating were observed in five of the six artefacts sectioned. These observations were confirmed by the hardness values which usually fell for the artefacts tested (Table 2). Currently recommended plasma operating temperatures have dropped still further from the 270°C used on these pieces, but we still believe that changes such as grain growth and altered hardness are likely to take place at lower temperatures, especially if the treatments are prolonged.

Silver

Two of the three silver artefacts treated were selected for metallographic investigation. These were a group

Table 3: Summary of SEM mapping of sulphur and chlorine in samples taken before and after plasma treatment.

Sample	Chlorine		Sulphur
	before	after	
935 strip	several maps; not significant	several maps; not significant	
936 silver coins	not significant	not significant	corrosion layers contain sulphur before and after
938 knife	present	present	
939 lynch pin	not found	present in one of two samples	
940 coulter	present	present	
942 silver bowl	present	present	not found before or after
945 lynch pin	present	present	
946 sickle	not found on sample areas	present	

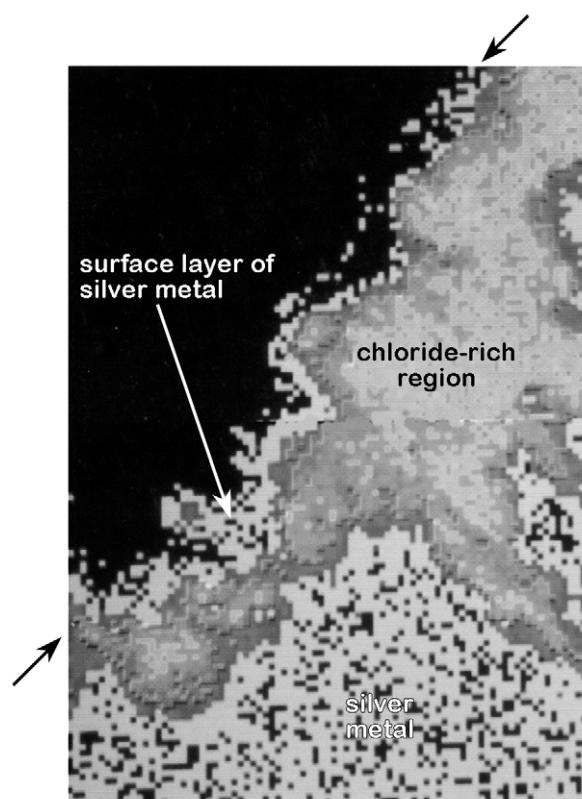


Figure 9: Distribution of chlorine in the corrosion of the silver bowl (1939, 10-10,8) after treatment. The chloride-rich regions are unchanged corrosion overlain with a thin layer of metallic silver from the reduction of the surface corrosion. The arrows show the approximate line of the original surface. Image height 900µm.

of silver coins held together by their corrosion, and one of the more corroded silver bowls from the Sutton Hoo burial. The sections were examined in the SEM and analysed by EDX. The corrosion of the coin group is made up principally of silver sulphide (Ag₂S) whereas that on the bowl is mainly silver chloride (AgCl), the familiar horn silver. Digital mapping of the sulphur and chlorine before and after treatment showed very little difference in the overall sulphur and chlorine contents (Table 3, Fig 9). The only significant change was the reduction of the corrosion on the outer few microns of the surface back to silver metal. XRD of samples taken from the corroded surface of the bowl also found silver chloride before treatment and silver chloride together with some elemental silver after treatment.

Neither of the two sections examined showed any evidence for the precipitation of copper at the grain boundaries. The copper content was about 3–5%.

Discussion

The plasma reduction and passivation or ‘nitriding’ processes lie, or rather lay, at the heart of the plasma

treatments. In the reduction stage the charged ions of the plasma either displaced ions such as chlorides or reduced hydrated metal oxides, such as goethite, $\text{FeO} \cdot \text{OH}$, back to the metal, or to a more reduced oxide such as magnetite, Fe_3O_4 .

Bradley *et al* (1997) noted that it was difficult to envisage the mechanism by which the very active plasma could penetrate into the corrosion layers without becoming discharged, and the results of our investigations now seem to be supported by other groups (Aoki *et al* 1993; Oswald 1997), who also reported that the actual chemical reactions are confined to the surfaces and the bulk of the anions, chlorides etc, remain untouched. In this respect the approach adopted by Sjøgren and Buchwald (1991) using the plasma in a DC mode, with the object to be treated as the cathode, and which operates at temperatures in the vicinity of only 100°C seems more promising.

What does seem to happen with the standard method is that the corrosion layer is rendered much more friable, specifically with extensive crazing or cracking of the surface, which in turn facilitates its subsequent removal by mechanical or chemical treatments. Rather worryingly, it is thus likely that the bulk of the chlorides removed will be from the outer corrosion layers, but as with the old washing methods, the damaging chlorides will remain untouched buried deep in the akaganeite against the iron metal core. It is also difficult to see how the plasma ions can bring about this cracking by the direct effect of discharging at the surface. Instead, it seems more likely that the indirect effect of local heating, coupled with the overall heating of the whole system in conditions of near vacuum for prolonged periods are the cause of the cracking by shrinkage brought about by dehydration. Oswald (1997, 135) came close to this conclusion, where he noted that 'No clear distinction can be made between purely thermal effects and the chemical effects of hydrogen plasma on corrosion products'.

Conclusion

Much early metalworking/heat treatment processes are very likely to have left the metal in a non-equilibrium, non-fully annealed state often with significant local variation where their structures were frozen in transitional states as the metal cooled. Evidence of these metalworking treatments and the associated low-temperature deliberate tempering are potentially put at risk by quite modest temperatures like those that were typical of the plasma process.

On the test pieces from the British Museum, the plasma treatment had little effect on the silver, and on the iron the results were equivocal. The artefacts were treated at temperatures that would be considered rather high by current practitioners, and which caused permanent change to the hardness and structure of the iron. The treatment did little to the corrosion beyond loosening it and, without the waxing treatment, the metal continued to corrode.

This work and that of others such as Arnould-Pernot *et al* (1994) does seem to show that it is not possible to stabilise iron by the plasma method at temperatures low enough not to affect the metallographic structure. Schmidt-Ott and Boissonnas (2002), having also ascertained that on test pieces the plasma treatment by itself was unsuccessful in eliminating active chlorides, now use a very gentle form of the treatment operating at temperatures as low as 80°C for six hours to loosen the corrosion. This considerably speeds up the subsequent alkaline sulphite treatment which really does remove the chlorides. However, it is by no means certain that these low level heat treatments have been universally adopted as the risks to the microstructure of the metals at higher temperatures have not previously been emphasised. As the plasma treatment is not actually necessary for the alkaline sulphite treatment to work, and as any form of heat treatment raises the subsequently unverifiable possibility that the metallographic structure may have been modified, it may be safest to take the final step and dispense with the plasma treatment altogether.

What can finally be said is that metallographers studying ancient metal artefacts need to be aware of how they were conserved, and take account of the effects of these treatments in interpreting the structures they see.

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