
REFRACTORIES: CERAMICS WITH A PURPOSE

Paul T. Craddock

*Dept. of Conservation and Scientific Research, The British
Museum, London WC1B 3DG*

Email: PCraddock@britishmuseum.org

Introduction

This paper is written from the view point of the user, expounding some of the requirements of a metallurgical refractory ceramic, and to some degree how these were met in antiquity, through a range of metallurgical operations. In this paper only extractive and refining metallurgy will be discussed. It is hoped to cover the ceramics associated with casting operations at the foundry in a subsequent paper. For more detailed petrological and mineralogical descriptions the reader is recommended to works such as those of Bayley (1992a), Rehren (2003), Freestone (1989), Freestone and Tite (1986), Freestone *et al.* (1991) and Tite *et al.* (1982a; 1982b; 1985; 1990). These publications also show how the scientific study of the vitrified and slagged remains can provide useful information on the materials and operating parameters of the early metallurgical processes.

For the early ceramicist, metallurgy must have presented a new range of problems and potentials beyond that required of the usual domestic pot that usually had to do no more than hold relatively small, light loads at temperatures that rarely exceeded 100 °C.

The primary requirements can be listed as follows:

- physical strength,
- the ability to withstand very high temperatures, and
- thermal robustness to accommodate thermal shock and steep thermal gradients.

In addition to these primary requirements, in some metallurgical processes the components of the ceramic body actually contributed to the chemistry of that process.

Previous studies (see above) have shown that in antiquity the clays used in metallurgical ceramics were

not particularly refractory - overall they tended to be made from the same clays as the contemporary domestic pottery. Freestone and Tite, in their excellent 1986 survey of ancient refractories, comment that 'their qualification for inclusion with 20th century materials of this class are often doubtful'. Large quantities of clay were needed for the furnaces etc. at the smelting sites, and to have brought special clays with superior refractory qualities would have added very significantly to the overall cost of the smelting operation. Some necessary properties could be conferred by the addition of a range of fillers (temper), notably crushed quartz or vegetal material, often in considerable quantities.



Figure 1. Fragment of a coil, massively tempered with chaff / straw, from a post-medieval lead-smelting furnace from Zawar, India (P.T. Craddock / British Museum).

In general strength and refractory qualities were not as paramount as they were to become in the Industrial Revolution and after, because early processes tended to be on a smaller scale, of shorter duration and often operating at lower temperatures. For example, Tylecote (1986: 99) noted that early crucible volumes tended to be small, typically of the order of 10s to 100s of cm³, only increasing to over 1,000 cm³ up to 1,500 cm³ in the late medieval and post-medieval period in Europe. The common clays used for ceramics tended to have significant percentages of metal oxides such as those of sodium, potassium, calcium, magnesium, and particularly of iron, which could react with the silica in the clay at the elevated temperatures necessary for many metallurgical operations, leading to the vitrification and slumping of ceramic bodies. However, as noted above, the relatively short duration of most processes meant that they could be completed before the ceramic container, be it furnace or crucible failed completely.

Although physical strength and ability to withstand high temperatures were in practice not always pressing problems, the ability to withstand thermal shock and steep thermal gradient within the ceramic was vital. A furnace or crucible that cracks in operation is not just useless, it is dangerous. In general theoretical considerations and experimental work have shown that large quantities of temper and low firing temperatures combine to give good resistance to thermal shock (Tite *et al.* 2001). Additions of large quantities of quartz temper seems to achieve the same result, at least in calcareous clays, probably by creating a system of micro cracks on firing (Kilikogou *et al.* 1998). Resistance to thermal shock and steep thermal gradients could also be achieved by having a very open structure, often achieved by the addition of large amounts of vegetal material, whether in the form of chaff (Figures 1 and 2) or as dung (London 1981; Gaimster 1986; Rice 1987: 407).

On firing this creates an open structure that is better able to accommodate the localised expansion caused by uneven heating, and such cracks that do occur will be stopped at the first void and thus not develop into a major failure.

These are some of the primary requirements of metallurgical refractories generally, what follows is a more detailed consideration of the ceramic requirements of specific metallurgical operations of smelting and refining.

Processes

Smelting

Furnaces in antiquity were necessarily small, 30 cm internal diameter being typical (Craddock 1995: 170). This was because they were normally supplied with air by humanly-operated bellows, or by wind power, neither of which could generate sufficient power to penetrate a larger area. The smelting charge through most of the furnace height will have been quite light, being composed mainly of charcoal, but in the lower regions the furnace walls will have had to be of sufficient physical strength to contain quantities of dense, corrosive liquid slag at high temperature in excess of 1,000 °C. In addition the operation is not a static one, more material was continually being charged, waste material removed, and even the operation of the bellows will have caused significant movement of the bellows tubes (*tybers*) which ran through the furnace wall. The walls could be up to

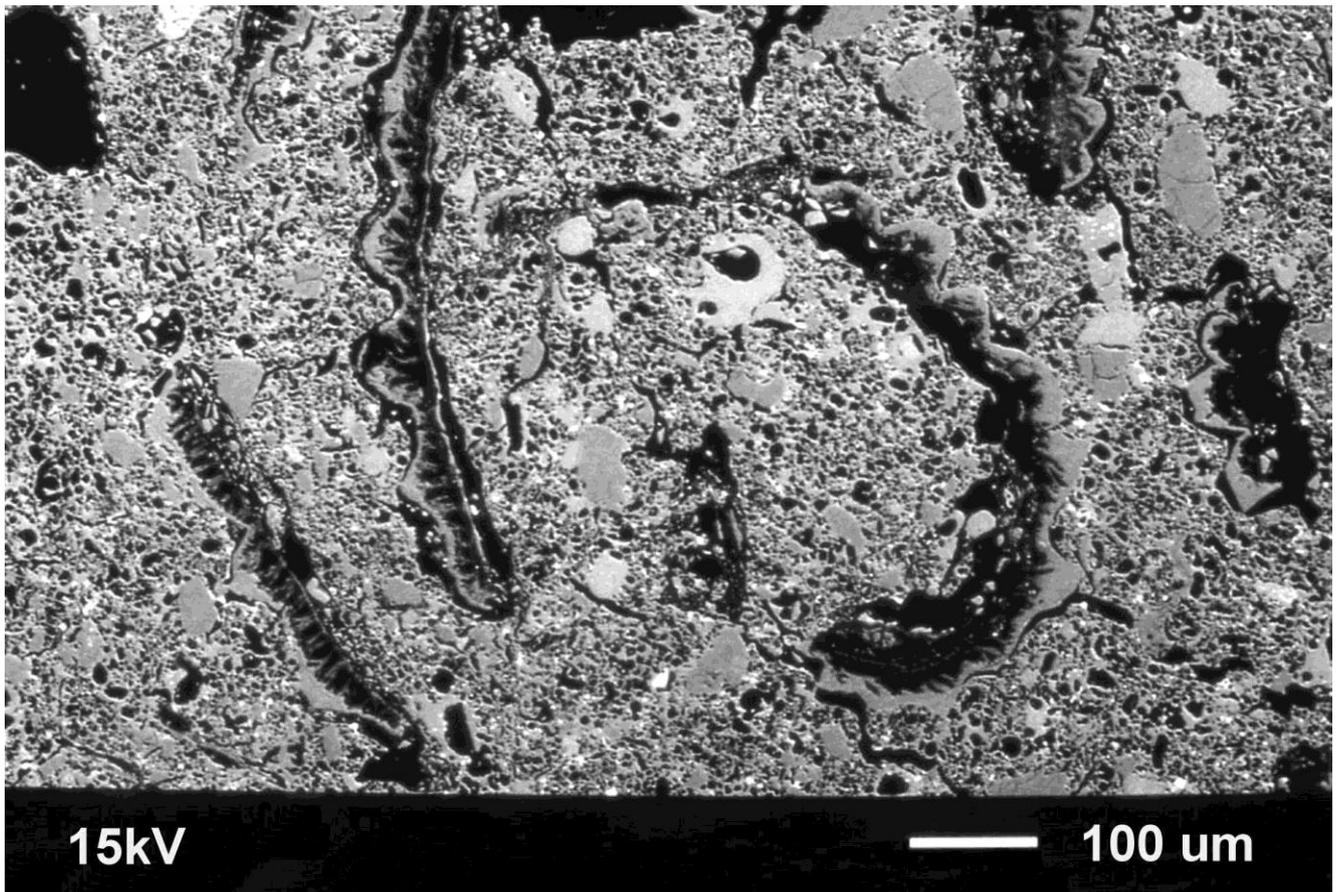


Figure 2. SEM backscattered electron image of a section through a Gattibosaballi crucible showing extensive voids left by the burning out of rice husks (from Freestone and Tite 1986).

30 cm thick, as evidenced by the foundations of some early iron-smelting furnaces (Crew and Charlton 2007), but were often much thinner, some being no more than 3 cm thick, especially towards the top (Figures 1 and 3). Additional support could also be obtained by building the furnace into a bank or by piling earth around the walls.

The thickness of the walls was also determined by the duration of the process. A smelting process of one to three hours (quite typical of early processes) could take place in a thin-walled furnace before heat loss by radiation from the furnace walls became serious, and a relatively short process would lose much heat by conduction in a thick-walled furnace especially of small diameter (Rehder 2000: 15-16). Conversely a long duration process (up to about 12 hours in antiquity) would benefit from the insulation provided by thick walls.

The ceramic of the thicker walls were often tempered with large quantities of relatively large fragments of the local rock, mine waste, crushed slag, straw/chaff



Figure 3. Section through a fragment of the wall of a post-medieval lead-smelting furnace from Zawar, India. The wall has been coil-built, two rather flattened coils are visible. Note the heavy slagging and vitrification on the right hand, contact side (P. T. Craddock / British Museum).



Figure 4. Section across a heavily tempered fragment of furnace wall from the Bronze Age smelting site at Timna, Israel. The black fragments are of slag, the white fragments are of quartz and the single bright red fragment is of grog (cf Figure 8; M.S. Tite / British Museum).

(the latter often in the form of dung) with little regard for refractory properties but providing a reasonably stable open structure (Craddock 1995: 169-74; Figure 4). The walls could be slab built, sometimes around a stone foundation and lower walls but the upper walls were often coil built and then fettled with clay on both the inside and outside (Figures 1 and 3).

At Zawar and at Dariba in North West India, the walls of the post-medieval copper and lead smelting furnaces were built of coils typically about 2-3 cm thick and where the internal and external lining survive, an overall thickness of about 4-6 cm. In addition to the chaff and dung temper it is clear that the coils were formed by rolling the clay around straws that were several cm in length and these were clearly orientated in the roll.



Figure 5a. Medieval zinc-smelting furnace at Zawar, still containing its last load of retorts (P.T. Craddock / British Museum).

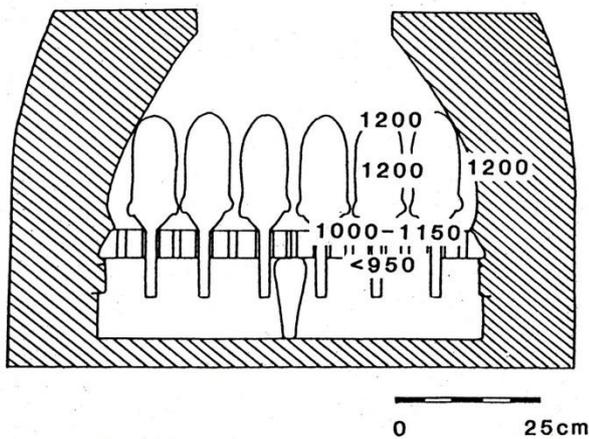


Figure 5b. Simplified diagram of section across the furnace shown in Figure 5a. The retorts sat upon large moulded perforated ceramic plates and the forming zinc vapour passed down in the small finely moulded condensers. The numbers refer to temperature estimates based on the vitrification of the refractories (B.R. Craddock / British Museum).

Overall there was some selection, even though the clays and to some degree the fillers were the same, there was a difference in the quantity and coarseness of the fillers. Thus for example at the Medieval zinc smelting site at Zawar (Craddock *et al.* 1998) (Figures 5a and b) where the refractories are of the local clays tempered with phyllite or slate mine debris and crushed quartz, there is a gradation in temper size from the furnace bricks to the retorts which sat on the moulded plates, which were next in fineness, down finally to the small, thin condenser tubes on the retort ends which were finest of all (Figure 6). To some degree this gradation was matched by the size of the piece from the large furnace bricks down to the thin, rather intricate condensers where the



Figure 6. Sectioned retort and condenser (bottom left). Note the large fragments of white quartz temper in the retort walls but the much finer structure of the condenser ceramic (A. Milton / British Museum).

plasticity of the clay would have been an important consideration in their moulding.

The tuyeres had special requirements, and posed special problems, they were of a delicate precise shape but had to withstand extreme thermal gradients. The ceramic tube could be made in several ways. A thin sheet of clay could be wrapped around a straight reed of the appropriate diameter until it was of the required thickness. This could then be withdrawn, or more usually left to burn out when the tuyere was fired. At Timna in Israel (Rothenberg 2000) the Late Bronze Age tuyeres were formed of several layers of clay interspersed by layers of thin reed to provide some longitudinal support (Werker 1990: 74 and Figs. 59 & 102; Rothenberg 1990: 29-37) and lengths of straw were clearly incorporated in some of the post-medieval tuyeres at Zawar (Figure 7).



Figure 7. Section across a fragment of a post-medieval tuyere from Zawar, India. Note the large number of small holes in the coil that were originally filled by straws lying in the plane of the coil (P.T. Craddock / British Museum).

Alternatively thicker tuyeres could be made by pushing a stick through a cylinder of well-tempered clay (Figure 8). Because of their relative thinness, tuyeres were of finer clays than the furnace walls through which they protruded (Figure 9, cf Figure 4).



Figure 8. Student on an experimental metallurgy course, making a tuyere by pushing a stick through a cylinder of clay, crude but effective (P.T. Craddock).

The tuyeres had to endure extremes of prolonged temperature gradient, not just along the length from inside the furnace out to the bellows but also over much smaller distance at the tip of the tuyere in the furnace reaction zone which could be at a temperature in excess of 1300° C but was delivering cold air. Once again an open structure enabled the



Figure 9. Section across a tuyere from the Bronze Age smelting site at Timna, Israel, with just a little quartz temper (cf. Figure 3; M.S. Tite / British Museum).

ceramic to survive this extreme temperature gradient without breaking. Tuyere failure through cracking is very rare, but most show heavy vitrification and erosion.

Erosion of both the tuyeres and of the furnace walls by the furnace charge was common and in certain cases may have been quite deliberate; the refractories acting as a slag former (Merkel 1989).

It is clear from the analyses of the slags from some smelting processes that they contain elements, especially aluminium, that are not present in any great quantity in the ore but are to be found in the refractory clays. It is possible that the clay may have been added as a distinct slag-forming flux, or alternatively have come from the furnace walls etc (Craddock *et al.* 2007). In some instances the refractories were quite deliberately incorporated. In the Mafa highlands of North Cameroon, for example, the rich iron ores were smelted until the recent past in an unusual process with huge tuyeres leading down from the mouth of the furnace to the reaction zone (David *et al.* 1989). There, the silica in

the clay of the tuyere reacted with some of the iron oxide ore to create a fayalitic, iron silicate slag, in which the reduced particulate iron could coalesce to form the solid iron ingot.

Refining

The product of the first smelting of many metals was highly impure, or at least sufficiently impure to render them unusable. The traditional refining practice, known as *fire refining* (Peters 1911: 530-77; Merkel 1990: 107-9), was to remelt the metal in an open crucible or hearth, exposed to the air and stir, whereupon many impurities would oxidise. Some of these, such as sulphur and arsenic, would be lost as vapours, others could react with the silica in the crucible or hearth, to form a distinctive slag, known as crucible slag (Tylecote 1986: 100-2). This is particularly relevant for the refining of copper. In the traditional process the first metal could contain several percent of both sulphur and iron. Fire refining would create sulphur dioxide and iron oxide. The latter could react with the clay of the walls of the container to form the slag which could then be easily skimmed off (Craddock 1995: 202-4).

More specialised refining processes for precious metals, included *cupellation* for silver and *salt parting* or *cementation* for gold, both of which required special refractory ceramics (Bayley 1992b).

In the cupellation process, and the closely related *scorification* process (Bayley and Eckstein 1997), the impure silver is wrapped in lead and heated to approximately 1,000 °C exposed to a strong air blast whereupon the lead and any base metal in the silver oxidise to form one phase, whereas the silver (and any other noble metals such as gold that it might contain) remain as molten metal and a separate phase (Craddock 1995: 221-31). Most descriptions of the process describe the lead phase as being mainly composed of just litharge, PbO, but in practice much of the lead is present as lead silicate, and in fact many ancient fragments of the reaction vessels, known as cupels, are mistakenly described as being litharge fragments, so thoroughly have they absorbed and reacted with the lead oxide (Bayley 1992a).

From Roman times onwards the cupels contained ash, particularly bone ash, in addition to the clay (Martín-Torres *et al.* 2009). The open structure of the calcined bone readily absorbed the forming metal oxides by a physical capillary action into the body of the cupel where it could react with the silica. Thus

again the metallurgical refractory in addition to having to contain the material, despite considerable thermal strain, also contributed to the chemistry of the process. N.B. bone ash cupellation is first found in urban workshops where silver was recycled, rather than in the primary mining sites where access to more specialised materials was more limited (Craddock 1995: 229, and see below for more on this aspect of refractory usage).

Gold usually occurs containing considerable quantities of silver and in antiquity gold was usually alloyed with silver. Thus it became necessary to devise a means of removing silver from gold, especially with the establishment of the concept of controlled composition after the introduction of coinage. This was first achieved by the Lydians at Sardis in the 6th century B.C. using salt cementation (Ramage and Craddock 2000), and the process became common throughout the Old World (Bayley 1991). In this process the finely divided impure gold was placed in layers in common salt contained within an ordinary domestic earthenware cooking pot and placed in wood-fired furnace (Figure 10). Here the temperature and nature of the ceramics were all important. The temperature had to be carefully maintained at about 800–900 °C for many hours, hot enough to vapourise the salt, but not hot enough to melt the finely divided gold.

The wood fire generated not just heat but also water vapour, which together with oxygen from the air could freely penetrate the open structure of the earthenware pot and permeate the reaction zone within. The combination of water and salt vapours under oxidising conditions produced a highly acidic vapour. Some of this reacted with the iron minerals in the earthenware to produce the extremely volatile and astringent ferric chloride, FeCl₃. This together with the HCl attacked the silver in the gold, creating a vapour of silver chloride, which dissipated and was absorbed into the ceramic parting vessel and furnace bricks, which were probably subsequently smelted to recover the silver (Ramage and Craddock 2000: Figs 5.41 and 5.49) leaving behind the now pure gold. Thus in this instance the open structure of the refractory was important as well as its composition. Much later, the eminent French scientist, Jean-Baptiste Boussingault, was working at the mint in Bogotà (Boussingault 1833, quoted in Ramage and Craddock 2000: 66-7), and carefully recorded the rather archaic process, using earthenware cementation vessels. He attempted improvements using impermeable stoneware 'Cornish crucibles',



Figure 10. Lydian gold-refining furnace at Sardis, Lydia, 6th century B.C. The earthenware pot containing the gold and salt sat on a pedestal in the wood fire. The open structure of the pot allowed air and water vapour to easily penetrate to the reaction zone inside the pot (P.T. Craddock / British Museum).

presumably of white, iron-free, kaolin clays, and discovered to his surprise and ‘the great satisfaction’ of the local workmen that no silver was extracted.

Gold parting with solid salts or with sulphur were increasingly replaced by treatments with mineral acids from the end of the Medieval period (Ramage and Craddock 2000: 69) but cementation was carried until the 19th century, and not just in Bogotà. Recent excavations in London have revealed evidence of both salt and sulphur cementation of gold alloys in the first half of the 19th century, not in regular workshops, but in a notorious slum, and probably connected with criminal activity (Dungworth 2012).

Crucibles were used for melting and for the refining of metals (Tylecote 1976: 16-19; 1986: 96-102; 1987: 183) and in some instances for the primary smelting (Zwicker *et al.* 1985; Rehren 2003; Rehder 2000: 104-8; Bayley and Rehren 2007) or alloying reactions such as the production of brass by the cementation process (Craddock 1995: 292-302; Bayley 1998; Rehren 1999) and the production of crucible steel

(Craddock 2003; 1998; Rehren and Papachristou 2003). The production of liquid steel was arguably the most severe challenge to refractories, requiring them to endure temperatures of the order of 1500 °C, way above the vitrification temperature of most clay bodies.

Steel, the alloy of iron with about 0.5-1.0% of carbon, was originally usually formed by some form of solid state carburisation or case-hardening process in which the solid iron was surrounded by a variety of carbon-rich materials and heated for long periods at high temperature in the hope that some of the carbon would enter the iron. The iron itself would have usually been made by a solid state process and would contain slag which seriously weakened it, and the carbon content of the steel produced by carburisation would have been rather heterogeneous, which was also a source of weakness. Melting the steel would allow the slag to be removed and the metal to become homogeneous, but the problem was developing a refractory that could survive the

melting temperatures of steel which lie in the region of 1400–1500 °C, depending on the carbon content.

The production of crucible steel seems to have begun rather over 2,000 years ago in the north India - Central Asia region (Craddock 1998). The Indian crucibles always seem to have been of ordinary, iron-rich clays, similar to those used in ordinary pottery production (Lowe *et al.* 1991; Freestone and Tite 1986; Figure 11). However they do seem to have had large quantities of vegetal material (Figure 2) and this, as well as contributing to the thermal stability of the ceramic, also dealt with the problem of the iron. The crucible steel-making process was intensely reducing condition, such that the vegetal materials in the crucible body were charred and reduced the iron oxides to globules of metallic iron, thereby significantly reducing the iron oxide content; Freestone and Tite (1986) estimated the FeO content had been reduced from about 5% to 0.5–1.0% in the samples they examined, and thus rendering the crucibles much more refractory.



Figure 11. Partly sectioned post-medieval crucible for the production of crucible steel from Gattibosaballi, Karnataka, with a partially formed steel bar, also sectioned, inserted into it (P.T. Craddock).

The high vegetal content meant that the resulting ceramic body was full of voids, very much reducing the physical strength, but as only a few hundreds of

grams of steel would be contained in the crucible and as the metal cooled and set in crucible this weakness would not have been a serious impediment.

A completely different approach was in use over a thousand years ago in Central Asia. There, for the first time, specially selected and highly refractory clays that were largely composed of silica and alumina and only minor quantities of the other metal oxides (Rehen and Papachristou 2003). These must have been difficult to work being somewhat aplastic, but were extremely refractory, refring experiments have shown that the crucibles made from them were stable at least to 1600 °C. The thin-walled crucibles were unaffected by the intense heat of the forming steel and thus have true refractory properties.

The crucibles have been found at several sites including Merv, in the south of Turkmenistan, dated to the 8th and 9th centuries AD (Feuerbach *et al.* 2003) and at Achsiket (Eski Achsy) in the Middle Fergana Basin of Uzbekistan, dated to between the 9th and 12th centuries AD (Papachristou and Swertschkow 1993; Rehren and Papachristou 2003). Thereafter the process seems to have declined, but crucible steel was still being produced Bukhara in the 19th century (Anosov 1841). At present the origins of this very advanced crucible steel technology are unknown as are the possible connection or influence that they may have had on modern industrial refractories.

Conclusion

As was made clear in the introduction, few of the ceramics used in extractive metallurgy in antiquity would qualify as refractories in modern usage. Usually local clays were used regardless of their refractory properties tempered with fillers such as crushed rock, vegetal material, grog or slag fragments. Yet these ceramics functioned well within the limitations of the processes concerned. By comparison with the industrial processes that commenced in post-medieval Europe, and in China somewhat earlier, the processes of antiquity were small-scale, short in duration and relatively low temperature. The small scale of operations meant that there was often difficulty in maintaining temperature and the ceramics were likely to be subjected to both thermal shock and steep thermal gradients. By the addition of large quantities of filler, especially of quite macroscopic pieces of chaff /straw either directly or as dung, the ceramics could withstand these stresses for the duration of the process. In practice most metallurgical ceramics

rarely survived more than one operation, before being discarded. Their vitrified and slagged fragments exist in quantity on the sites of early metallurgy for the ceramicist and metallurgist to study and reconstruct the operating parameters of the processes concerned.

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