High temperature performance of two-layered ceramics and the implications for Roman crucibles

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ABSTRACT

Roman metalworking crucibles are frequently characterised by an extra outer layer (EOL) of clay, applied to a pre-formed vessel. Three-point bending and standardised dead-weight loading tests were conducted to determine the advantages offered by the EOL. Deformation and fracture behaviour, at temperatures up to 1,100°C, of two-layer, monolithic, and tempered-monolithic briquettes were compared. Measurements indicate that the two-layer briquettes are more resistant to fracture at high-temperatures: above 850°C they show more extensive plastically deformed regions than monolithic briquettes. The influence of temper is consistent with previous results: tempering causes quasi-stable fracture and reduced fracture strength. Results suggest EOLs assisted in preventing catastrophic failure.

Keywords: Roman crucibles, multi-layer ceramics, mechanical properties, high temperature performance

INTRODUCTION

Studies of ancient ceramic objects suggest that the artisans who made them frequently developed an empirical understanding of their materials, and were able to make decisions concerning raw materials, paste preparation and fabrication techniques which improved the performance of their products (e.g. Braun 1983; Freestone and Tite 1986; Braekmans *et al.* 2017). Arguably the most challenging conditions encountered in the ancient world were those associated with metallurgy, where the ceramics had to withstand exceptionally high temperatures, contact with molten metals, and rapid temperature changes, frequently under high loads. In pre-Roman periods, the high demands of metallurgical processes led to the modification of traditional bodies through the addition of various types of temper to the clay to improve performance, such as quartz sand and/or organic material (Howard 1983; Bayley and Rehren 2007; Hein *et al.* 2007). Only later does the careful selection of refractory clays for ceramic production become evident (e.g. Freestone and Tite 1986; Martinón-Torres et al. 2006, 2008). The present paper deals with the apparent advantages offered by a particular ceramic technology which is characteristic of Roman metallurgy, but which is largely unremarked outside the specialist literature: the use of two-layer ceramic bodies (e.g. Bayley and Rehren 2007; König and Serneels 2013; Gardner 2018).

The Roman period saw major advances in technology and the empirical understanding of materials appears to have improved significantly. Metalworking crucibles clearly demonstrate such developments. A recent large-scale study of Roman crucibles from Britain (Gardner 2018) along with other published works (Rehren and Kraus 1999; König and Serneels 2013), reveal the common practice of Roman metalworkers using wheel-thrown crucibles with an additional layer of clay applied to the external surface. While they appear most frequently in the Roman period there is also some evidence of pre-Roman two-layered crucibles (e.g. a Late Chalcolithic example from Iran (Thornton and Rehren 2009)) and the continued use of this technology into the medieval and post-medieval periods (e.g. Martinòn-Torres and Rehren 2002; Thomas 2006;Thomas 2013).

Despite the prominence of such two-layer crucibles, there has been limited discussion on the function of the second layer in the literature. Those who have focused on this issue suggest that the EOL insulated the crucible, protecting it from thermal shock (Bayley *et al.* 2001; Martinón-Torres & Rehren 2002; Bayley & Rehren 2007; König & Serneels 2013). Bayley and Rehren (2007, 50) provide the most detailed discussion, describing EOLs as 'sacrificial layers' that provide insulation, whilst still being relatively conducting due to their glassy nature, increasing thermal capacity and protecting against thermal shock. They also suggest that these layers had the potential to seal cracks within the main crucible body and also protect the main vessel from the fluxing ash, from the bed of fuel that the crucibles would have sat in.

The arguments put forward by Bayley and Rehren (2007) are well-founded in principle but no systematic investigation has been completed to test them, though recent experiments by Furger and Helfert (2018) have begun to explore different paste recipes described in medieval treatises. Clearly all of the phenomena listed would be advantageous to a Roman metalworker, but how important were they? This paper outlines and discusses the results of an experimental project that set out to investigate the influence of these EOLs on the mechanical properties of crucibles.

BACKGROUND

Archaeological material

Roman wheel-thrown crucibles were predominantly made of white-firing ceramics. It is generally assumed that metalworkers acquired pre-fired vessels from local pottery industries and applied EOLs, made from local red-firing clays. In some cases there is even evidence to suggest that specific forms were made for industrial purposes, for example a form identified within the Oxfordshire White Ware repertoire (W73 of Young 1977) is described as a crucible, and evidence for the production of Ebor Ware in forms specifically for the glass industry in York have also been identified (Cool et al. 1999). However, there are also examples of 'domestic' forms being re-purposed as crucibles, for example small wheel-thrown Verulamium ware lamps used as crucibles in London (Gardner and Marshall forthcoming), and Nene Valley colour-coated ware beakers at Vindolanda (Gardner 2018). This indicates that there were likely different modes in place for acquiring wheel-thrown vessels for use as crucibles in the Roman period.

EOLs are common features of crucibles used mainly, though not exclusively for the melting of copper-alloys, . Typically, the EOLs are thicker on the base and come up to the rim where they are much thinner, as illustrated in figure 1a and 1b. The EOLs were applied to pre-fired vessels and this secondary layer was likely fired during use in metallurgical processes. Macroscopically they vary in appearance, but all appear heavily vitrified. Some have a very glassy appearance, whilst others are more matt. Depending on the redox conditions and the process in which the crucible was involved, the colours of the EOLs also vary considerably from buff browns to pinkish reds, through to black (see figure 1). A number of crucibles from Roman London have been assessed (Gardner

2018) and multiple examples show macroscopic cracks within the EOLs, caused by clay shrinkage, (e.g. figure 1d) whilst others have a much smoother appearance (e.g. figure 1c). Also present are charcoal impressions and/or relict charcoal fragments on the base of a number of the crucibles with EOLs. These impressions imply that the EOL became soft enough to mould over the charcoal beds the crucibles sat in (e.g. figure 1b).

Microscopically EOLs of used crucibles invariably show continuous vitrification with large bloating pores (40 to >100μm). The inner layers of the crucibles are typically less vitrified. The interfaces between the EOL and inner crucibles were also examined and some of the EOLs show merging boundaries (e.g. MOQ10[1807]<604>, figure 2) while others have more defined boundaries with voids forming at the interface (e.g. Vindolanda SF.5983, figure 2). The merging boundaries indicate that the EOL and crucible are chemically bound, whilst the clear boundaries indicate that their binding is discontinuous.

Elemental analyses have also shown (König and Serneels 2013; Gardner 2018) that the EOLs are typically made from a less refractory clay than the inner vessel, often displaying higher iron oxide concentrations, and in some cases also higher lime contents. The lower refractoriness of the EOLs helps to explain why they are often more vitrified than the inner vessels, an effect further enhanced by their direct contact with the embers. The crucibles were externally heated and therefore the EOL was in direct contact with the heat source, typically charcoal for this period. Fuel ash from charcoal is rich in fluxing elements such as Ca and K. Equally, there would be a temperature gradient from the external to internal surfaces due to the low thermal conductivity of traditional ceramic materials (Müller *et al.* 2013; Müller 2017).

Materials testing and archaeology

Over the past decades, a number of projects (more recently e.g. Hein *et al*. 2015; Müller *et al.* 2013;2015) have outlined the factors which impact on the thermal and mechanical properties of archaeological ceramics. By testing experimental briquettes, which had been designed on the basis of practices observed in the manufacture of archaeological pottery, it has been possible to determine the effects of the addition of temper, the type of clay and the firing temperature on the properties of archaeological pottery, helping to answer archaeological questions about aspect such as technological choices. However, these and other previous experiments (e.g. Bronitsky and Hamer 1986; Feathers 1989; Feathers and Scott 1989; Hoard *et al*. 1995), assessed material properties of such model archaeological ceramics only at room temperature. As archaeological crucibles are used at relatively high temperatures, it is important to consider the effect of elevated temperatures.

Theoretically, increased temperature results in the ceramic becoming ductile and eventually performing plastically, which results in lower fracture strengths at high temperatures (Kingery *et al.* 1976). Davidge (1979, 17, figure 1.13) provides an idealised model for the dependence of ceramic strength on temperature. He identifies three general regions with different fracture behaviour. In the lower temperature region, fracture is always brittle and occurs within the elastic region without any measurable plastic deformation. At intermediate temperatures (the level of which varies greatly with type of ceramic) fracture is still brittle but takes place after a small amount of strain, perhaps a few tens of a percent. Finally, at higher temperatures, fracture may occur after appreciable plastic deformation of the order of 10% or more.

However, crack blunting by atomic slip does not occur in ceramics even at high temperatures but the plastic strain measured is the result of a large number of microcracks emanating from the region around the crack tip (Davidge 1979, 101) and/or movement of dislocations around the same region (Rice and Thompson 1974), relieving the stress at that point. Whatever the mechanism, there is consensus that at high enough temperatures, ceramics behave effectively plastically, and extensive deformation occurs in strength testing prior to fracture (Kingery *et al.* 1976). Therefore, theoretically during use crucibles are less likely to catastrophically fail due to brittle fracture, but more likely become ductile and potentially plastic depending on their composition, deforming with applied stress instead of fracturing.

Mechanical properties of multi-layered ceramics

An important consideration, specific to the material studied here, is how the layering of ceramics impacts on mechanical properties. Since the beginning of the 1990s, multilayered ceramic composites have successfully been developed and studied (Clegg *et al.* 1990). These multilayered ceramics were inspired by biometric studies of shell and teeth (Sánchez-Herencia *et al*. 2009; Eichhorn *et al.* 2005) and have been used in a number of different applications, including armour (e.g. Sands *et al.* 2009) and dental veneers (e.g. Sadaqah 2014). These multilayered ceramics were developed to overcome the low toughness and lack of failure reliability of 'monolithic' ceramics (Clegg *et al*. 1990; Minatto *et al.* 2015). A key feature that imparts improved mechanical properties is the ability of multilayered ceramics to deflect cracks leading to higher effective strain during deformation resulting in improved ‘flaw tolerance’ (Sánchez-Herencia *et al*. 2009), albeit by sacrificing some fracture strength.

In general, laminar ceramic composites are distinguished by the strength of their interfaces which determine the energy absorbed during fracture, i.e. their effective toughness. Weak interface composites are produced by either inserting thin layers of low strength material (e.g. a graphite-type material) between the ceramic layers or by ensuring that the coherency between the ceramic layers at the interface is low (Clegg et al. 1990). The weaker layers cause any propagating cracks to deflect and encourage delamination of the layers. Such behaviour results in increasing effective toughness as there is a higher dissipation of energy at these points and the overall failure is non-catastrophic (Dey et al 2008). The stress-strain graphs for such composites show sequences of crack-arrest steps (Clegg et al. 1990).

On the other hand, strong interfaces are produced by combining two ceramics with strong coherency (Sbaizero and Lucchini 1996; Minatto *et al.* 2015, Sánchez-Herencia *et al*. 2009). Thermal expansion mismatches between the layers create residual compressive and tensile stresses in alternate layers during cooling which encourage localised microcrack generation and propagation as well as crack deflection and bifurcation which also prevent catastrophic failure. Such multilayer composites show improved effective fracture toughness and final flexural strength in comparison with monolithic materials.

MATERIALS AND METHODS

Materials

A series of experiments were devised to investigate the impact of the EOL on the mechanical properties of clay-based ceramic crucibles. As archaeological material is subject to alteration through use and subsequent burial it cannot be used reliably to investigate such effects. Instead, tests were carried out on a series of experimental briquettes, manufactured using clays of similar chemical composition to the Roman crucibles from London and their EOLs as determined by Gardner (2018). The briquettes were manufactured in a controlled manner, meaning that the results are reproduceable.

For the production of the test briquettes, a commercial, white-firing, alumina rich clay (REF, Ramfos_245) containing fine quartz inclusions was chosen to simulate the white-firing, wheel-thrown crucibles (table 1). REF is more refractory than a typical earthenware although it would not be considered refractory in modern terms. A second, less refractory, clay (KAL) was chosen to replicate the EOLs with a much higher iron and lower alumina contents. Its composition is closer to the Earth's average alluvial clay as determined by Kamber *et al.* (2005). KAL was collected from Kalami, Crete, as raw clay and required some processing. It was soaked for 48 hours, aggregated by mixing and the largest inclusions were removed by hand. KAL has previously been used in a series of thermal and mechanical experiments by the Demokritos group (e.g. Hein *et al.* 2008; Müller *et al.* 2015). The elemental composition, determined by WD-XRF (Georgakopoulou *et al.* 2017), of both REF and KAL are shown in Table 1.

To produce the experimental briquettes, a series of experiments were initially carried out to attempt the addition of EOL to various pre-fired ceramics using methods potentially used by Roman metalworkers. After repeated failures, it became apparent that the joining of the two layers was not going to be successful using pre-fired base ceramics (i.e. the “inner crucible”). Two key problems were identified: (1) the fired ceramic absorbed water from the wet clay, drying it rapidly before the EOL had a chance to bond and causing it to fall away; (2) At the same time, the drying shrinkage of the wet clay caused it to shrink away from the pre-fired briquettes, damaging cohesion, and forming cracks (like those identified on archaeological examples, as seen in figure 1). In view of the difficulties caused by using a pre-fired ceramic, the two-layer briquettes were produced by joining the two layers of clay (one for the ceramic and one for the EOL) while still wet and then firing them together. This created satisfactory bonding between the two layers, replicating the archaeological examples with strong interfaces, but not those with weak interfaces. It is therefore likely that the two-layer specimens made in this way correspond to the second type of multi-layered ceramic described as strongly interfaced. Not only were the interfaces found to be chemically bound, but also different shrinkage rates of the two clays employed resulted in one being in tension and the other in compression.

Briquettes using the two clays were manufactured using the same methodology as Müller *et al*. (2016, 521). A special two-part mould for the briquettes was produced in order to control the thickness of the two layers. The briquettes were then fired and cut into test bars with the required dimensions (6 x 6mm thick and about 60mm long) and sanded to ensure the surfaces were flat and parallel. As the archaeological EOLs and crucibles were often heavily tempered, a series of REF briquettes were produced with varying loadings of quartz sand temper to investigate the influence of rigid inclusions on their high-temperature mechanical behaviour (table 2). Two different loadings of fine (125-250μm) and coarse (250 - 500μm) sand at 10% and 30% were added to the plastic clay (equivalent to 12% and 35% dry weight addition) and incorporated by hand, ensuring homogeneity through repeated wedging. All briquettes were fired at 950°C (at a heating rate of 200°C/hour and a soaking time of one hour), selected to correspond to the previously estimated firing temperature of the wheel-thrown wares prior to their use as crucibles in Roman London (Amicone and Quinn, 2016).

Experimental procedures

The two-layer test bars were tested with the white REF ("internal") layer under compression to replicate the loading of the crucibles. Samples with clearly identifiable macroscopic flaws were not measured. Table 3 lists the different material sets, and the tests completed on them.

Fracture strength

Fracture strength was measured at room temperature (RT) in three-point bending tests on test bars using an INSTRON universal tester, with a cross-head speed of 100 μm/min. The measurements were repeated on 3 specimens of each test bars type. Three-point bending tests were also undertaken on each set of material at elevated temperatures (700, 800, 850, 875 and 900°C), using an INSTRON universal tester with a customised external furnace. The fracture strength σ_f (in MPa) was calculated using the following equation:

$$\sigma_f = \frac{3P_{max}s}{2bd^2}$$

where P_{max} is the maximal load in N, s the span of the support rods, b the width, and d the height of the specimen. Ultimate strength was also noted when this was higher than fracture strength. Ultimate strength is used to describe the maximum load-bearing strength of the material.

Standardised weight loading tests

Standardised weight loading tests are a more qualitative method of assessing the load-bearing capacity of a material and a way of simply comparing different samples of the same and different materials (Kingery 1976, 708). In this test, a fixed load is applied to the sample (30g in this case) and the temperature increased to 900, 1000, and 1100°C. These tests do not discriminate between deformation mechanisms. However, crucibles would have had a relatively constant or static load and therefore this method is, perhaps, more representative of actual usage. The amount they deformed was recorded and each specimen compared.

SEM imaging

A Hitachi S3400N scanning electron microscope (SEM) was used to image the fracture surfaces and any cracks created by three-point bending tests. A number of different acquisition modes were employed to best image the specific features identified. The samples were not resin-embedded, but were carbon or gold coated to improve image quality.

RESULTS AND DISCUSSION

Influence of layering

Fracture strength at room temperature

The monolithic briquettes showed typical brittle fracture at room temperature, with the characteristic single load-loss fracture peak expected of vitrified monolithic ceramics. The behaviour of the 50:50 briquettes in three-point bending tests on the other hand was more varied. The load displacement graphs of 50:50_RT1 and 50:50_RT3 show the same single load-loss fracture peak as the monolithic (see figure 3 for example). However, 50:50_RT2, shows two load-loss fracture peaks (figure 3).

The fracture strengths (table 4) for the two monolithic ceramics and the two-layer briquettes are comparable, with the finer REF clay slightly stronger than KAL (when excluding the sample where a macroscopic flaw caused early fracture, REF_RT2). There is, however, a higher degree of variation with the 50:50 briquettes, likely caused by the introduction of flaws during the layering process, as shown for example in figure 5.

Fracture strength at high temperature

The results of the three-point bending tests at elevated temperatures show that the ultimate and fracture strengths increased substantially with temperature (figure 4). At 900°C however, the fracture and ultimate strength decreased, with the exception of KAL at 900°C, where a further increase of ultimate strength was observed. The load displacement curves and fracture strength graphs in figure 4 show that for both monolithic and two-layer briquettes the ceramic became ductile at 875°C. At 900°C, larger displacements are evident due to the quasi-plastic deformation of the ceramic briquettes. Figure 4 shows that at 900°C the monolithic REF briquette showed a much shorter region of elastic strain than at 875°C and plastic deformation began much sooner. The plastic deformation continued to greater displacements until the sample fractured. This is also indicated by the difference in the ultimate and fracture strength of the REF briquette (figure 4 top-left). Figure 4 shows the results of the same experiment on a monolithic KAL briquette. KAL showed similar trends to the REF briquette; there were, however, differences. KAL at 850°C and 875°C exhibited lower fracture strength than REF and also appeared to deform less plastically. However, at 900°C, although the fracture and ultimate strength were still lower than REF, the displacement was much greater. The plastic deformation continued for longer before the briquette fractured in the same way. The 50:50 briquette showed very similar behaviour to the REF briquette up to 875°C (figure 4). However, at 900°C the two-layer briquettes showed a markedly different behaviour. The briquettes continued to plastically deform for much longer than the monolithic briquettes, eventually reaching the limit of the equipment (figure 4). It is likely that these 50:50 briquettes would show even greater displacement until they eventually broke, if the capacity of the equipment was greater.

Observation of the localised microstructure of the experimental briquettes was carried out using SEM, to assess the physical manifestation of the applied strain. There were no significant findings in the monolithic briquettes. However, the 50:50 briquettes subjected to three-point bend testing at 900°C showed a network of micro-cracks in the bottom layer (KAL) (figure 5a), which was under tension during the bending tests. These cracks concentrate around the load point of the briquette, but do not travel past the interface of the two layers. Imaging of the bottom (KAL) (figure 5b) and top (REF) layers (figure 5c) further demonstrates that the cracks are only present in the bottom layer.

Influence of tempering on fracture strength at high temperatures

Monolithic REF briquettes with added quantities of temper (table 2) were subjected to the same high-temperature three-point bending tests described in section 3.2.1. Room-temperature testing was not carried out as the impact of temper on fracture behaviour has previously been investigated extensively (e.g. Kilikoglou *et al*. 1995; 1998; Hoard *et al.* 1995). Figure 6 summarises the effects of temper on fracture behaviour at elevated temperatures. The load displacement curves of the briquettes tested at 800°C indicate that, like the un-tempered monolithic REF briquettes, brittle fracture occurred, and the pure REF briquettes are stronger than the tempered examples.

At 900°C the briquettes showed different behaviour. The monolithic briquettes with added temper showed pseudo-ductile behaviour and stable, instead of brittle, fracture (excluding REF_12C which broke in a brittle manner as did the untempered REF). During testing the briquettes did not break, as illustrated by the load displacement curves (Figure 6). The briquettes did however, break on cooling with the exception of one, REF_12F. This sample's fracture surface was examined with SEM and imaging of the crack showed that there were a number of strands or threads of a glassy material bridging the gap (figure 7). This demonstrates that the glassy phases within the briquettes had softened to the extent that they stretched. The bridging of gaps within the ceramics, by these glass threads, would have resulted in additional fracture energy dissipation which would have delayed the final fracture. Other mechanisms may also have been active, such as interlocking.

Comparison of the results for tempered briquettes with those of un-tempered REF briquettes indicates that the tempered ceramics became more ductile at 900°C. The results suggest that the strength reduced between 800 and 900°C in the tempered briquettes. The test bar with 12% coarse temper, REF_12C, showed similar behaviour to the un-tempered sample, and, unlike the briquette with 12% fine quartz sand, broke in a brittle manner. An explanation for this might be that for the same amount of added temper (wt.%), the coarse ceramics will have a much lower number of inclusions per unit volume than the ceramic with fine temper. Therefore, the probability of a propagating crack encountering an aplastic inclusion in its path is much lower in coarse tempered than fine tempered ceramics. Kilikoglou *et al.* (1995) showed that the addition of around 20%, or more, aplastic inclusions results in an interconnected network of so-called 'damaged zones' causing the dissipation of energy and a slower, more stable, fracture at room temperature. The result of the present high-temperature tests appears to show that the same process is effective at 900°C, and may contribute to the observed fracture behaviour of the highly tempered test bars.

Standardised weight loading

The results in table 5 show the displacements of the bars at 1,000 and 1,100°C. It is possible to observe the distinct differences in behaviour of the briquettes at the different temperatures. At 900°C the briquettes remained flat, at 1,000°C there was slight deformation and at 1,100°C there was considerable deformation. Table 5 shows that the three different types of briquette deformed to a similar extent at 1,000°C, with KAL showing slightly more displacement than the REF and 50:50 samples. At 1,100°C there was higher differentiation between the briquettes. KAL deformed the most, then REF and finally 50:50 which deformed c. 2 mm less than the KAL briquette. KAL deforms more since it is less refractory than REF. The deformation of the tempered briquettes started at 100°C higher than the un-tempered examples as the body is stabilised by the anchoring effect of the added quartz inclusions.

The addition of temper to REF showed varying results. The addition of fine temper resulted in considerably less deformation than the pure briquettes and also less than those with coarse temper, which appeared to deform more at 1,100°C than the pure briquettes (table 5). This is probably because the fine temper—which has a higher number of inclusions per unit volume than the respective coarse tempered—effectively stabilises, or 'anchors', the matrix. Furthermore, the fine temper reduces the extent of glassy-phase deformation which is the predominant mechanism for the pseudo-plasticity observed. Coarse temper on the other hand has a much less pronounced effect so the pseudo-plastic deformation measured is comparable to the materials without temper. Equally, coarse temper introduces elongated voids (Müller *et al.* 2010) which are likely to contribute to increased deformation.

SUMMARY

Two-layer ceramic briquettes made of a layer of refractory clay and a layer of low refractory clay have been shown to be more resistant to fracture at high temperatures than single-layer ceramics of the same materials. At high temperature the briquettes effectively become ductile and behave pseudo plastically, and two-layer briquettes show much longer regions of plastic deformation than the monolithic samples. This is probably due to a combination of effects. Firstly, both the monolithic and two-layer briquettes have softened at the high temperatures and crack-blunting and crack-arrest becomes possible. In the monolithic samples the number of micro-cracks increase till they weaken the briquette and cause fracture. However, in the two-layer briquettes these micro-cracks appear to build up in the same way but only in the less refractory layer which is under the most tension during testing, suggesting that the interface between KAL and REF is preventing their propagation.

The testing of monolithic REF briquettes with varying quantities and coarseness of added quartz sand has shown that temper impacts on the materials properties at high-temperature. Room temperature experiments have previously been completed in reference to archaeological material and indicate that, at high enough quantity the addition of aplastic temper causes stable fracture (Kilikoglou et al. 1995). This is equally the case at high-temperature. Increasing temper to matrix ratio progressively lowers the ultimate strength of the ceramic. For the same quantity of temper, the finer fraction is more effective at stabilising than the coarse. The cracks are arrested at the quartz-matrix interface which dissipates some of the energy. The fracture energy is also dissipated by the plastic flow of the glassy phase and the added porosity by the addition of temper.

ARCHAEOLOGICAL IMPLICATIONS AND CONCLUSIONS

The results of these experiments show that there are a number of potentially significant benefits in the application of an EOL of low refractory clay and suggest that Roman metalworkers had an empirical understanding of material properties. The results show that, through a combination of mechanisms, the EOL protects the crucible from catastrophic failure. At temperatures above 875°C (in principle, these temperatures could be lower in reducing atmospheres—primarily, due to the transformation of Fe_2O_3 to FeO, a reactive flux (Maniatis and Tite 1975)—which these crucibles would have been used in) a clay-based ceramic becomes effectively ductile, tougher, and stronger. In most archaeological samples, the EOL is less refractory than the inner part (König and Serneels 2013; Gardner 2018), and these effects would have therefore manifested sooner, in the EOL, before they occurred in the inner, more refractory, part. Indeed, the EOL often shows complete vitrification and evidence, for example the impression of charcoal pieces, shows the material was soft during use, whereas the inner part of the crucible shows lower stages of vitrification. The presence of a softened, and therefore plastic EOL would have prevented cracks, initiated by impact, thermal shock, or stress of handling, from propagating through the whole vessel wall. Hence the EOL would have effectively prevented potential failure of the crucible. It is likely that these benefits would have been increased with decreasing refractoriness of the EOL, particularly because the degree of softening of the EOL would extend to lower temperatures, especially in reducing conditions, increasing the temperature range over which the vessel was protected.

There is evidence that crucibles have, at least occasionally, been reused. Since residual stresses would likely be relieved anytime the EOL was heated above the glass transition temperature, we would not expect an incremental build-up of residual stresses, with repeated re-use of crucibles. The putative advantage of thermal capacity and heat retention requires additional confirmation; however, this may have also impacted on their function and the decision of Roman metalworkers to apply the second layer. Overall, this experimental study suggests that EOLs provided significant benefits to the Roman metalworker; it likely improved the durability of the crucible at high temperatures and preserved its contents.

These more durable two-layered crucibles were used across the Roman Empire for the melting of copper alloys, and on occasions other metallurgical processes too. Whilst this was a widely used practice, Roman metalworkers sourced the inner vessels in different ways; using specific wheel-thrown forms in some instances and the 'domestic' forms in others. Difficulties encountered in the preparation of double-layered ceramic briquettes for the present experiments suggest that the application of the EOLs was likely not a straightforward task. Roman craftspeople had an approach to successfully achieve this which we do not yet fully understand. Finally, it is difficult to ascertain how many of the beneficial properties were actually understood by Roman metalworkers without completing further experiments which more closely model the actual conditions of early metal-melting. However, it is likely that in comparison to the handmade, and often less refractory crucibles of the pre-Roman periods, these would have been significantly superior; explaining their geographically widespread use and continued use into the medieval period.

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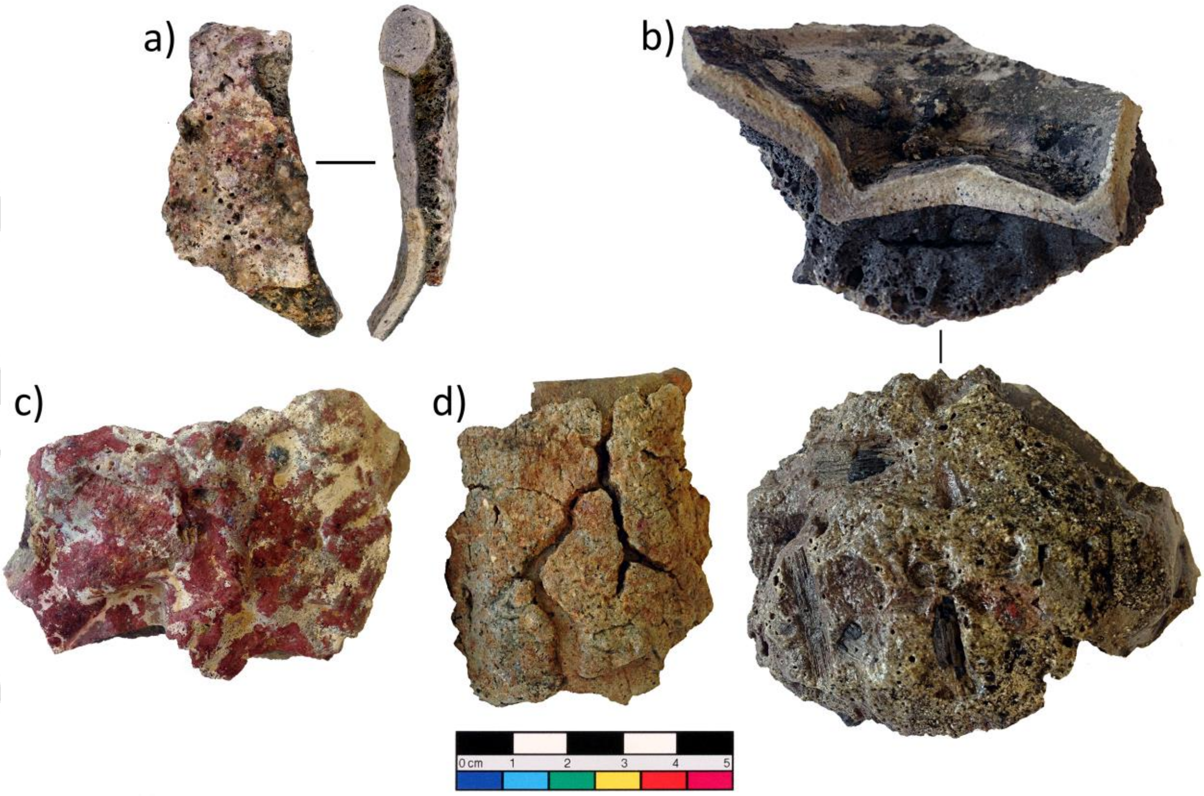

Figure 1: Archaeological examples of EOLs on wheel-thrown crucibles from Roman London: a) rim sherd GSM97[6900]<973>; b) base sherd BZY10[3092]<2562>; c) body sherd BZY10[2342]<2062>; d) rim sherd BZY10[2102]<962>. Photo reproduced by courtesy of MOLA.

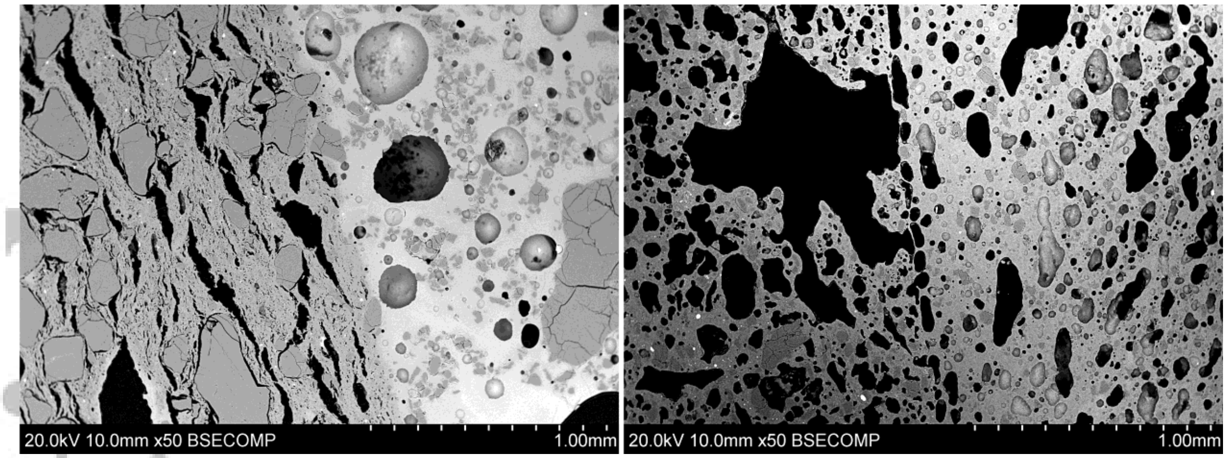

Figure 2: BSE photomicrographs of polished cross-sections of Roman crucibles and their EOLs. Left MOQ10[1807]<604>: example of a merging boundary (strong interface) between the crucible and its EOL and right (Vindolanda SF.5983): example of a clear boundary (weak interface) between crucible and EOL (EOL on right hand side of both images).

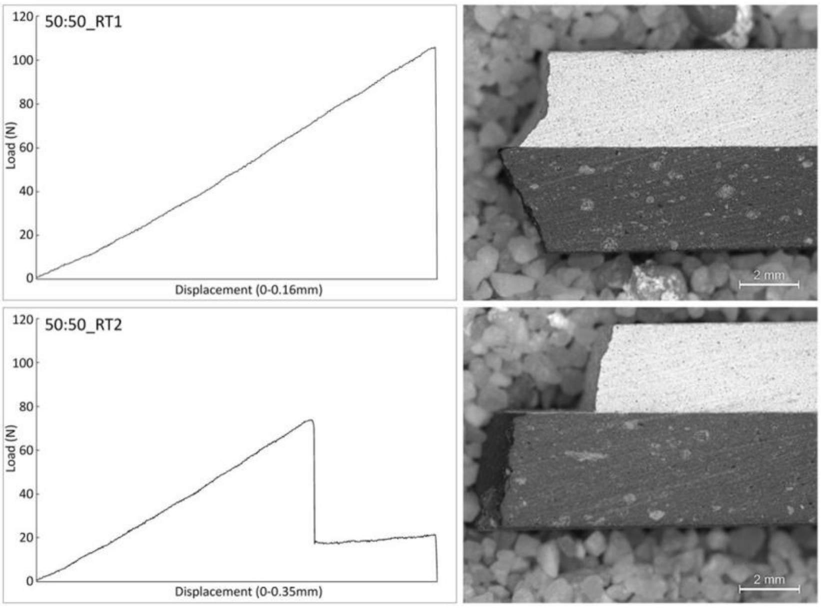

Figure 3: Load displacement curves for the three-point bend tests carried out on 50:50 test bars at room temperature with corresponding photos of the fractured specimens.

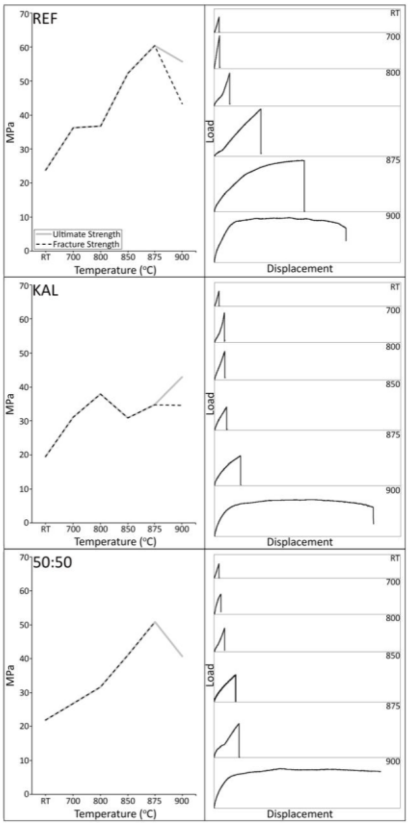

Figure 4: left: fracture and ultimate strength of briquettes subjected to three-point bending at increasing temperatures, right: the load displacement curve for each temperature for the (top to bottom) REF, KAL, and 50:50 briquettes.

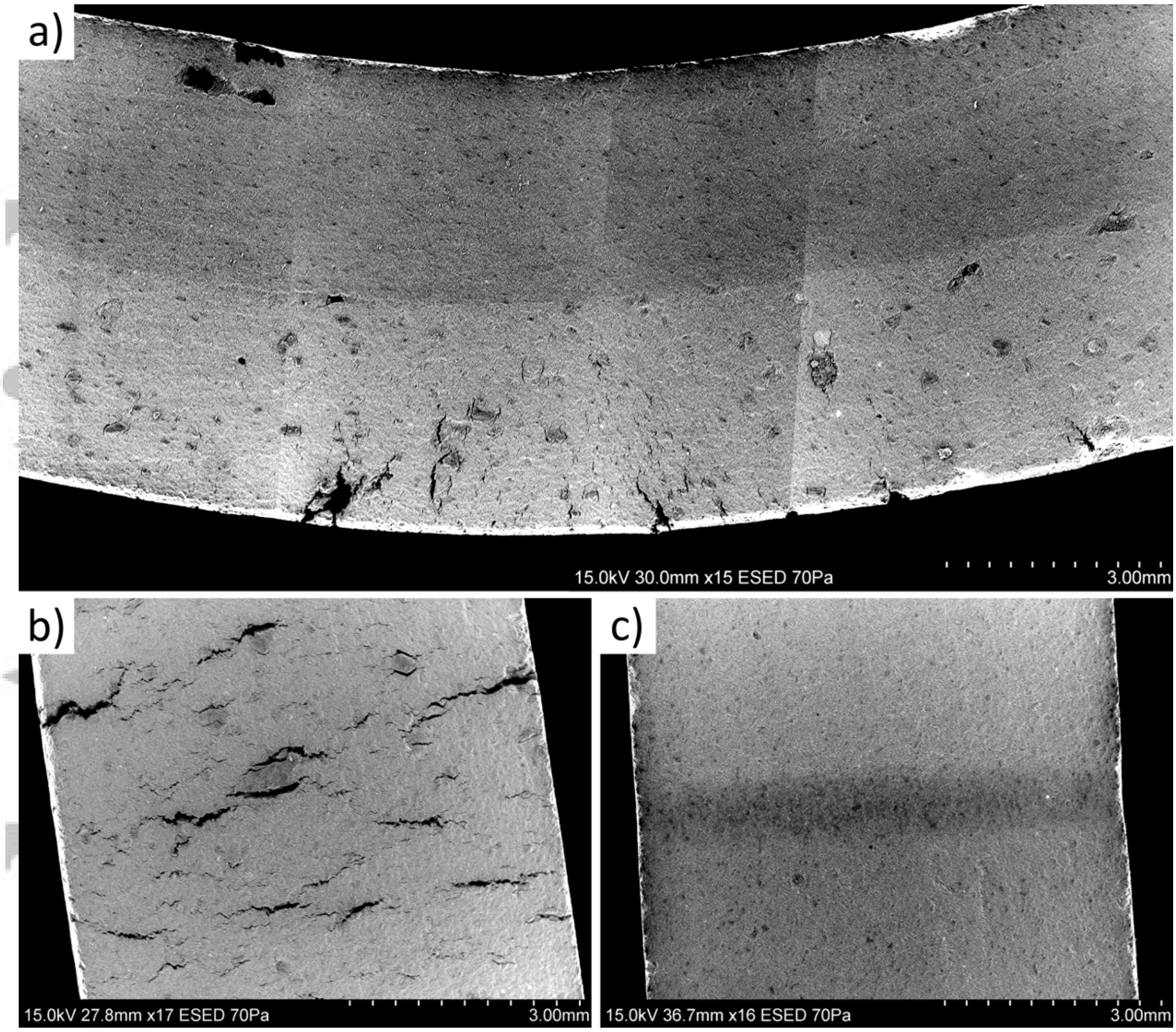

Figure 5: Secondary electron (SE) imaging of the 50:50 briquette which was subjected to three-point bending at 900°C (a. side view, b. bottom (KAL), and c. top (REF)).

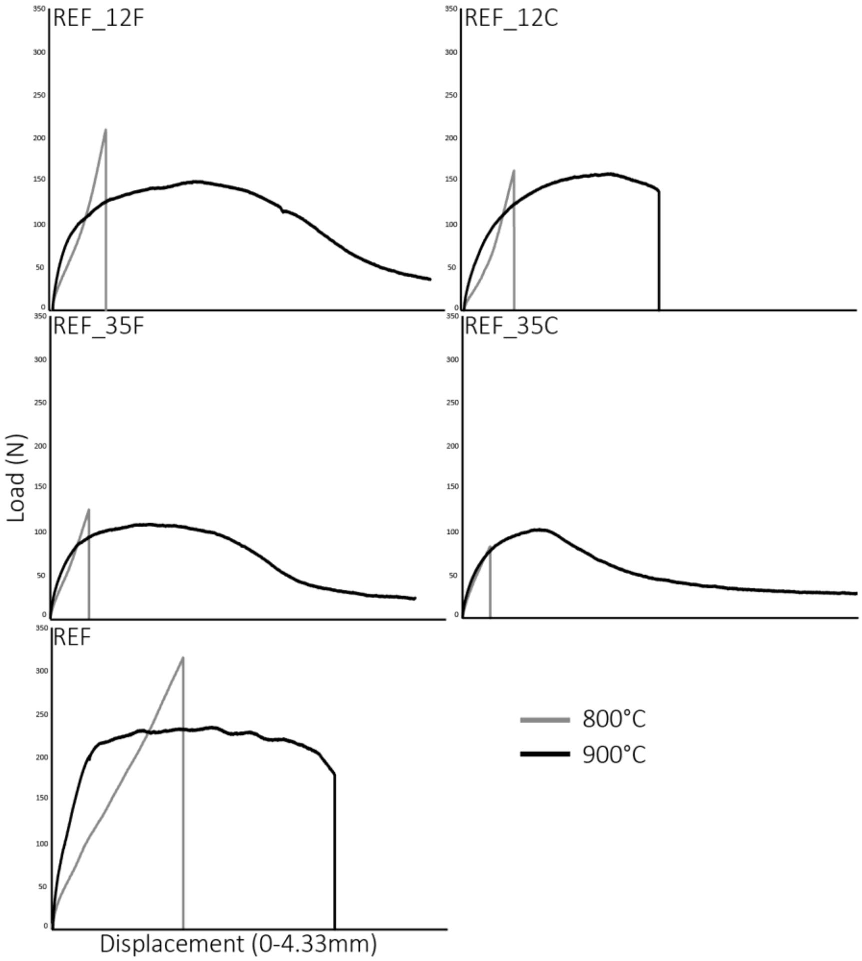

Figure 6: load displacement curves of three-point bend tests of tempered briquettes at 800°C and 900°C.

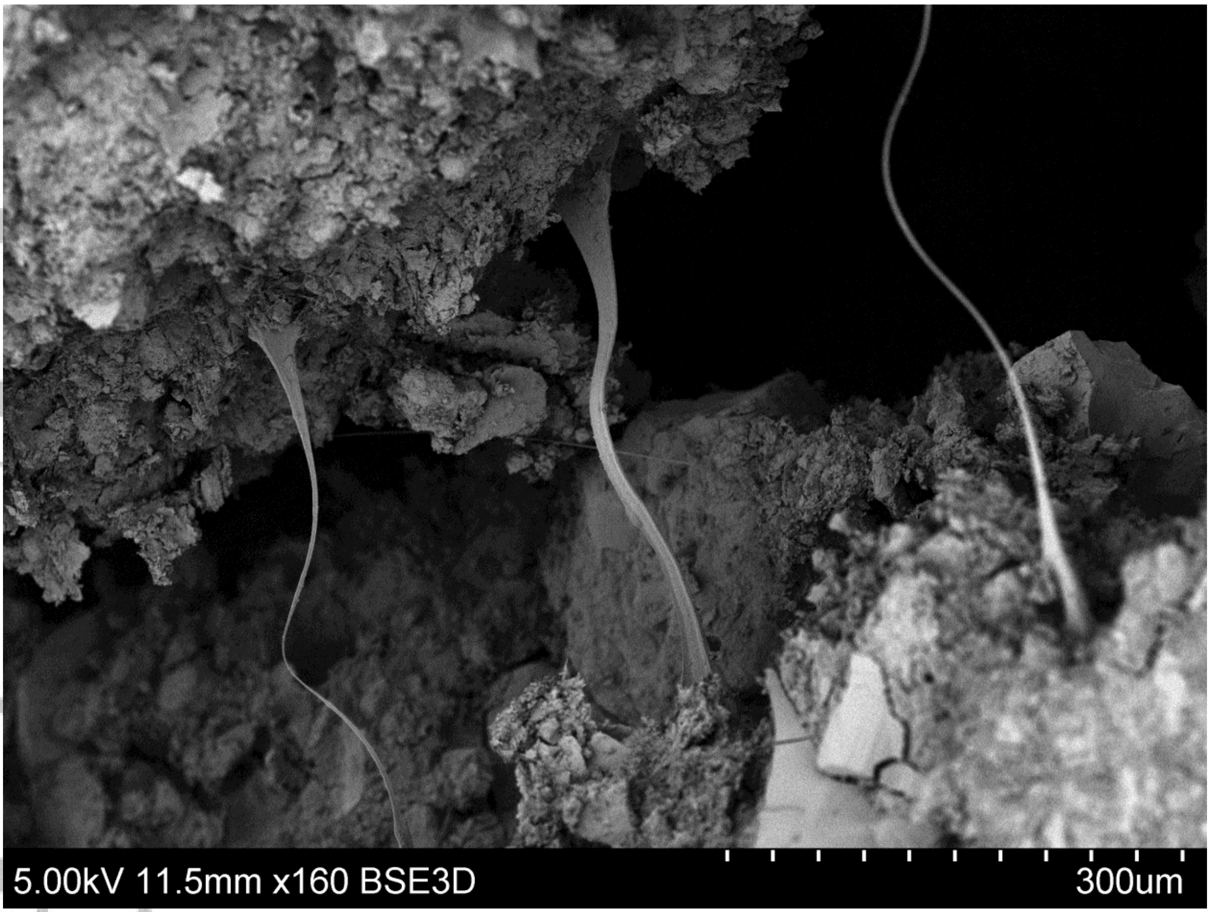

Figure 7: Glass threads bridging the crack in sample REF_10F (three-point bending at 900°C)

Table 1: Major elemental composition of the two clays as used (numbers in wt.%).

Clay	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	MnO	Fe2O3	LOI	Sum
REF	1.5	0.4	21.4	66	0.1	3	0.5	0.9	<0.1	0.8	5.31	99.97
KAL	0.9	0.7	17.1	63.2	0.1	2.1	0.7	1.2	0.2	8.3	4.74	99.51

Table 2: Briquettes with added inclusions and their sample identifiers

Material	Briquette identifier
Monolithic REF	REF_[temperature]
Monolithic KAL	KAL_[temperature]
Two-layer briquette	50:50_[temperature]
REF with 10% fine sand inclusions	REF_12F
REF with 30% fine sand inclusions	REF_35F
REF with 10% coarse sand inclusions	REF_12C
REF with 30% coarse sand inclusions	REF_35C

Table 3: table showing the tests completed on the different sets of materials (RT=room temperature; HT=high temperature; SWL=standardised weight loading test).

	RT three-point bend	HT three-point bend	SWL
REF	X	X	X
KAL	X	X	X
50:50:00	X	X	X
Tempered REF		X	X

Table 4: Results for the fracture strength (in MPa) measured for the three monolithic specimens at room temperature testing, alongside notes on the individual specimen

Repeat	50:50	Notes	KAL	Notes	REF	Notes
1	22.6	Small flaw at interface	20.6	-	25.1	-
2	16.4	2 step failure, flaw in KAL	19.1	-	10.8	Flaw causing early fracture
3	26.6	-	18.9	-	22.5	-

Table 5: Displacement measurements (in mm) from the standardised weight loading test

	REF	KAL	50:50	REF_12F	REF_12C	REF_35F	REF_35C
1,000°C	1.3	1.5	1.3	-	-	-	-
1,100°C	3.7	4.9	3	1.9	4.3	1.9	4.8