From the macroscopic to the microscopic: some scientific insights

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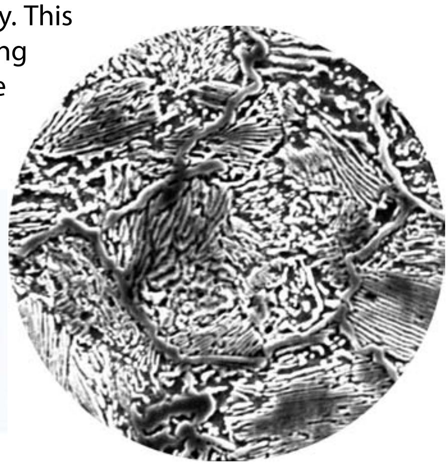
Metallographic and metallurgical studies help to give insights into the history of technology of metal artefacts. Debris associated with pre-industrial metallurgical activity is found in piled up mounds at sites which are referred to as slag heaps. Slags refer to the waste or by-products from the process of extraction of metal from the ore by smelting which is a pyrometallurgical process of reduction of ore to metal in a heated furnace. Slags are typically partially vitrified or in a glassy state as a mixture of oxides and silicates with minor remnants of entrapped metal. The lighter viscous slag separates from the metal and is usually tapped out of the furnace, characterised as tap slag. Tuyeres refer to the blowpipes or nozzles used to generate a draught to work the furnace.

In the bloomery process for smelting iron, a solid state iron bloom was produced; whereby the reduction of ore to iron metal took place at a temperature sufficient to reduce the ore and below the melting point of iron. Bloomery iron has a low carbon content, below about 0.04%, and this was used as wrought iron after a smithing process. In the blast furnace however, higher temperatures and more reducing conditions were reached, resulting in the formation of cast iron with higher carbon contents, going up to 2-4%, although this is a more brittle product. Crucible steel has an intermediary composition between wrought iron and cast iron, of about 1-2% carbon, classifying it as an ultra-high-carbon steel and has properties of high ductility for forging and high impact strength, making it highly suitable for weapons. It seems that in parts of southern India crucible steel was produced by a process of carburising wrought iron to hypereutectoid high-carbon steel as described by Srinivasan (1994, 2007) from Melsiruvalur in Tamil Nadu. This has also been described as the Mysore process at sites such as Gatihosahalli as noted by KNP Rao (1989) and Craddock (1998) and described by Buchanan. On the other hand, crucible steel processes reported from parts of Andhra Pradesh such as Nizamabad are thought to have followed co-fusion or melting together of cast iron and wrought iron to get a steel of intermediate composition as described by Voysey, also known as the Deccani process which has been studied especially by Thelma Lowe (1990). The term wootz derives from the word for steel *ukku*, which may be linked to the Tamil word, *uruku* (i.e. boiling) and such terms may hark back to classical Tamil Sangam literature (c. 300 BCE-300 CE) (Srinivasan 1994).

The ethnographic record in the Telengana bears some evidence of its long tradition of skilled metal processing and metal smithy. To get an idea of the kinds of finished metal artefacts found locally, a knife typically used by the community of toddy tappers in the Telengana region, to extract toddy from the palmyra palm, was investigated at the Indian Institute of Science using metallographic and microscopic study. This knife was collected by S Jaikishan and presented to S Ranganathan. Scanning electron microscopy (SEM) was undertaken on a polished cross-section of the blunt edge of the knife as seen in (Fig. 1). This is a back-scattered electron image which gives an idea of the different phases or constituents in the

Fig. 1 Broken toddy tapper's knife from Konapuram, Nizamabad district with scanning electron microscopy image of microstructure of blunt edge (Dept of Materials Eng., IISc)



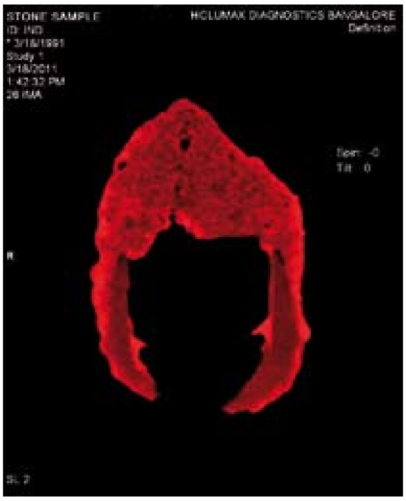


Fig. 2 CT scan slice across a crucible from Konasamudram, used in the production of crucible steel showing distinct layers of lining and luting (Indian Institute of Science, Bangalore)

metal, since the higher atomic number constituents show up brighter. The structure is clearly one of a high-carbon steel showing a network of cementite around hexagonal grains containing a matrix of lamellar pearlite (which is a mix of lower carbon ferrite and higher carbon cementite). The microstructure suggests that the carbon content is about 1-1.5%, with a characteristic structure associated with wootz steel, and such a structure is also found in a nail from Pattanam, (c. 1st century) in Kerala, excavated by KCHR (Srinivasan 2007). The Damascus blade forged of wootz steel has attracted the interest of modern material scientists in topics such as nanotechnology and superplasticity (Ranganathan and Srinivasan 2006).

Sites of crucible steel production can be distinguished by the presence of scattered broken crucible fragments left behind after the fired and intact crucibles were broken to retrieve the steel ingots. A range of analytical techniques were explored to gain more insights into the kinds of end products and the production mechanisms. One such was the medical imaging technique CT scan or Computed Tomography undertaken with the co-operation of Sajeev Krishnan, Centre for Earth Sciences at the Indian Institute of Science. A series of two-dimensional images or slices through a 3-dimensional object (i.e. a tomogram) is obtained. This is useful for non-destructive examination of heterogeneous materials like crucibles. Figure 2 shows a CT scan slice across a crucible from Konasamudram used in the production of crucible steel (location 10-2-10(2)). The different layers in the make-up of the crucible can be seen, including an inner, more homogeneous layer forming the wall of the crucible and an exterior heterogenous layer which forms a luting or covering around the inner layer. The heavily packed lid also has a large cavity in it which may have been the region through which the tongs may have been pierced to get a grip on the crucible, for example to remove the crucible once the firing cycle was completed after the ingot had formed.

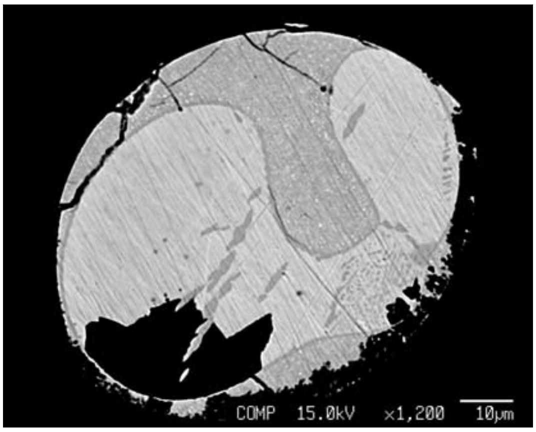


Fig. 3 Back-scatter electron image, using EPMA at CSM, University of Exeter, of green glassy slag from Waddad village showing metallic prills with structures resembling cast iron

An important study has been initiated with the use of Electron Probe Micro-analysis (EPMA-WDS) on some of the slags and crucibles undertaken in co-operation with the Camborne School of Mines (CSM), University of Exeter. In this technique a beam of electrons is fired at a polished metallurgical sample and the characteristic X-rays are analysed. This technique also enabled precise 'spot' analysis of the different phases and constituents. It was possible to analyze the glassy constituents and metallic remnants separately using a programme of separate standards and calibrations for each, one for oxides and the other for metals, and each measuring about 17 constituents including major, minor and traces. From preliminary investigations, one trend that is noteworthy is the growing evidence for the fairly well entrenched pre-industrial use of more efficient high temperature processes as seen from the finds of very 'efficient' slags and crucibles with very little metallic content left behind in them, and the evidence of very tiny globular 'prills' of ferrous metal remnants of less than 10 microns diameter. These suggest that temperatures approaching those needed to make iron molten; the melting point of iron, which is around 1500°C, can be lowered to about 1200°C under highly reducing conditions. For example, figure 3 indicates that glassy green slag from the village of Waddad in the survey area seems to have metallic prills or remnants that resemble the structures of cast iron. The lighter phase seen in the ferrous metal prill contained phosphorus-rich regions of up to 11%; iron phosphide is typically found in cast iron. This specimen also had a high calcium oxide content, up to 25%; limestone is continuously added as a flux in blast furnaces. Although blast furnace

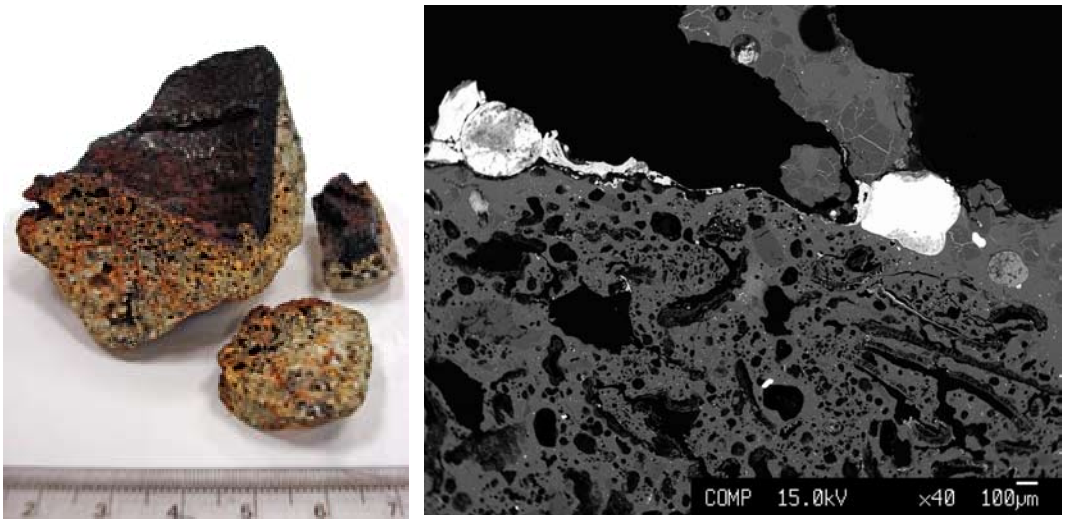


Fig. 4 Fragments of a steel-making crucible with back-scatter electron image of a section (TS-35), undertaken using EPMA at CSM, University of Exeter

technology is typically associated with China, this suggests that the prevalence of this technology in the pre-industrial Indian context may also need to be more thoroughly explored.

Some insights into the making of the crucibles for steel production could also be gained. It seems that the inner wall described before was especially well packed with rice hull relicts. These, when charred, would have contributed to the reducing conditions and refractory properties, being rich in carbon and silicon. In contrast, the outer luting or covering of the crucible had much more of quartz or siliceous fragments which seems to have been intentional to make the outer layer more refractory, as quartz has a high melting point, to enable the crucible to resist melting down. This is a trend also noted in some other studies on south Indian wootz crucible processes mentioned before by Lowe (1990) and Srinivasan (2007). The outer luting in particular in certain specimens was also seen to contain minerals like zircon, or zirconium silicate, confirmed by EDAX, and is reported to be found in sands in Andhra Pradesh, especially beach sands on the east coast. Zircon itself is used in modern metallurgical purposes and is described as a super-refractory material with a very high melting point. Of course, further bulk analysis would be needed to assess the proportion of such minerals in the fabric of the outer luting. Figure 4 shows a section of a crucible from crucible steel production showing entrapped ferrous metal remnants along the lining of the crucible, which is more siliceous and glassy, while the inner wall of the crucible is packed with several charred rice hull relicts in the matrix. Zirconium rich minerals are represented by tiny bright specks. Figure 5 is a dotmap for the relative elemental concentration of silicon across this section highlighting some of these aspects.

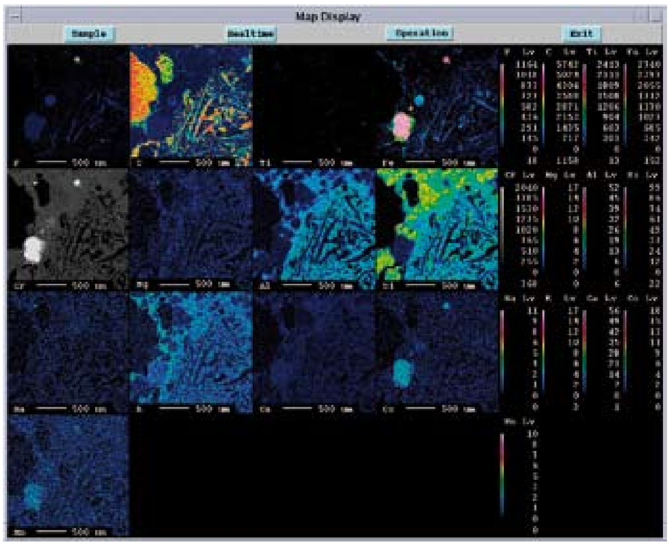


Fig. 5 Elemental concentration maps across section of crucible (TS-35) for P, C, Ti, Fe, Mg, Al, Si, Na, K, Ca, Co, Mn; undertaken using EPMA at CSM, University of Exeter

Further investigations are underway on ore specimens at Camborne School of Mines. Explorations are also being made on attempting to date sediments using Optically Stimulated Luminescence (OSL) dating with five samples collected in collaboration with CP Rajendran, associated with Indian Institute of Science and given to Wadia Institute for study. Investigations are also being made in collaboration with Research Laboratory for History of Art and Archaeology, University of Oxford.