Report on the examination of blue material from industrial remains at Warmley

Introduction

Brass is known to have been produced by cementation at Warmley Brass Works (Grid Ref ST 66992 72823) in addition to which zinc is known to have been produced by distillation. Rubble infill near the remains of a furnace at the Warmley site included fragments of a stony material notable for its blue colouration in varying degrees. There were suspicions that this colour resulted from the presence of zinc in some form, an indication possibly first referred to by Galon in the late 1740s when describing techniques of brass production at Namur.

A sample of the materials was examined by x-ray diffraction, and a polished thin section was prepared and examined by optical microscopy and a Scanning Electron Microscope (SEM).

Chemical analysis of the sample in the SEM (Table 1, Col. 1) showed it to contain around 40 wt.% zinc oxide, ZnO, 10% Al_2O_3 and 50% SiO_2. Neglecting the zinc oxide, the analysis corresponds to a siliceous fireclay, low in fluxes such as FeO, MgO, CaO and K_2O (Table 1, Col. 2). Fig. 1 shows the microstructure of the sample. Large ceramic fragments, about 1 mm diameter and relatively low in zinc, are set in a white matrix containing approximately 60 wt. % ZnO. The matrix also contains common sub-angular quartz grains, around 0.1mm diameter. More detailed examination of the low-zinc fragments (Fig. 2) shows that they contain grains of zinc spinel, $ZnAl_2O_4$ with subordinate zinc orthosilicate (willemite), in a matrix of silica and a potassium silicate glass. The zinc-rich compounds are concentrated around cracks and voids in the low zinc fragments (Figs. 1, 2). The $ZnAl_2O_4$ is often enclosed or rimmed by Zn2Si04, suggesting that the silicate phases formed after the spinel. The high zinc matrix is composed predominantly of $ZnSiO_4$. The composition of the matrix, excluding quartz grains, is given in Table 1 col. 3 and recalculated zinc-free in Table 1, col. 4. It again corresponds to a fireclay, this time less siliceous because the quartz particles have been excluded.

Table 1

	1	2	3	4	5	6	7
SiO_2	49.0	80.3	23.6	59.7	2.6	27.7	72.2
TiO_2	0.6	1.0	0.7	1.8	1.1		1.5
Al_2O_3	10.5	17.2	13.7	34.'7	52.6		10.9
FeO	0.9	1.5	1.1	2.8	0.5	3.3	0.8
MgO	0.2		0.4	1.0	0.9	0.9	0.2
CaO	0.2		0.2				1.8
K_2O	0.4	0.7	0.2				6.8
ZnO	39.0		60.0		41.6	66.9	3.6

1. Large area SEM/EDXA analysis of ceramic.

2. As 1. recalculated to 100%, neglecting ZnO.
3. Analysis of Zn-rich matrix, excluding quartz grains.
4. As 3. recalculated to 100%, neglecting ZnO.
5. Zincian spinel, $ZnAl_2O_4$. NB SiO_2 may be interference from matrix.
6. Zinc orthosilicate, Zn_2SiO_4. Interstitial glass phase.

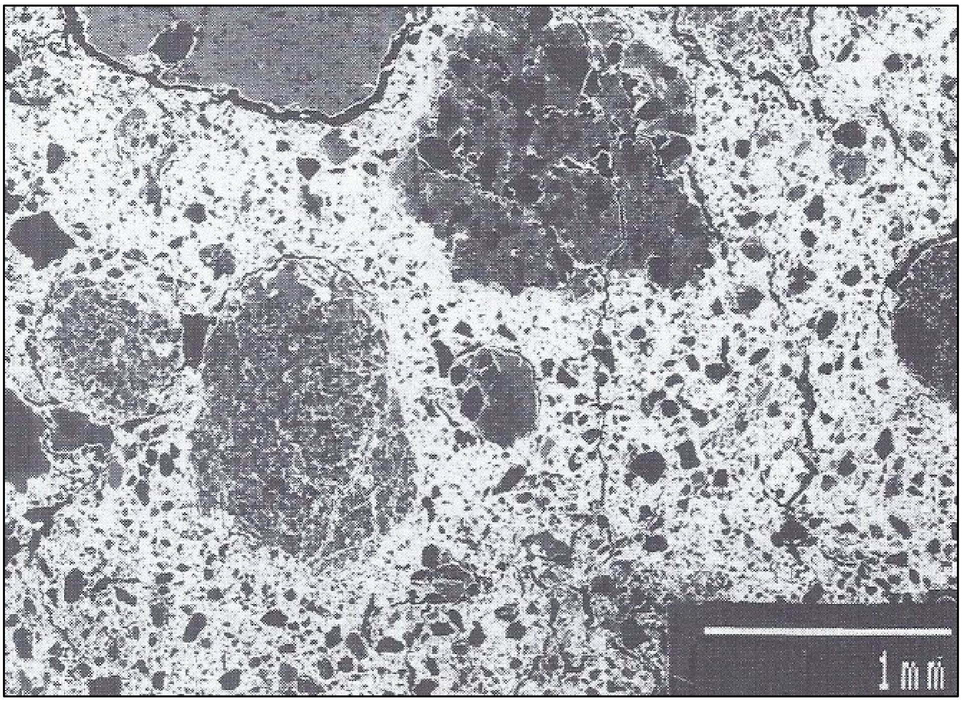

Fig. 1 SEM photomicrograph showing overall structure of ceramic. Large dark areas are relatively poor in zinc; note concentrations of zinc show white along cracks. Matrix is rich in zinc and contains numerous fine quartz grains (black) (Robinson back-scattered electron detector).

Interpretation

The sample appears to have been a fireclay ceramic which has been permeated by zinc vapour during use. Initially zinc spinel formed followed by zinc silicate. In the porous ceramic matrix, reaction has proceeded to the extent that most of the original fired clay material has formed zinc compounds. However, in less porous areas of the ceramic (possibly grog filler, or more likely mudstone fragments which are common in some fireclays) the impregnation proceeded less rapidly, and is at an early stage relative to the ceramic matrix.

The ceramic is likely to have been either a crucible used in brass cementation, or a zinc distillation retort. It is unclear which, but on at least some fragments of a cementation crucible copper contamination would be expected. None was detected in the present case but a single example is not conclusive. The sample appears to match the expected composition of a distillation retort; for example, Smith (1918) notes that zincian spinels were formed in retorts during use. A further possibility is that the ceramic represents a fragment of furnace brick or lining; this is less likely, as the furnace would have been isolated from the bulk of the zinc vapour by the crucible/retort containers. However, repeated use at high temperatures over very long periods of time might have resulted in such a material being formed. At present we are limited by the lack of comparative material.

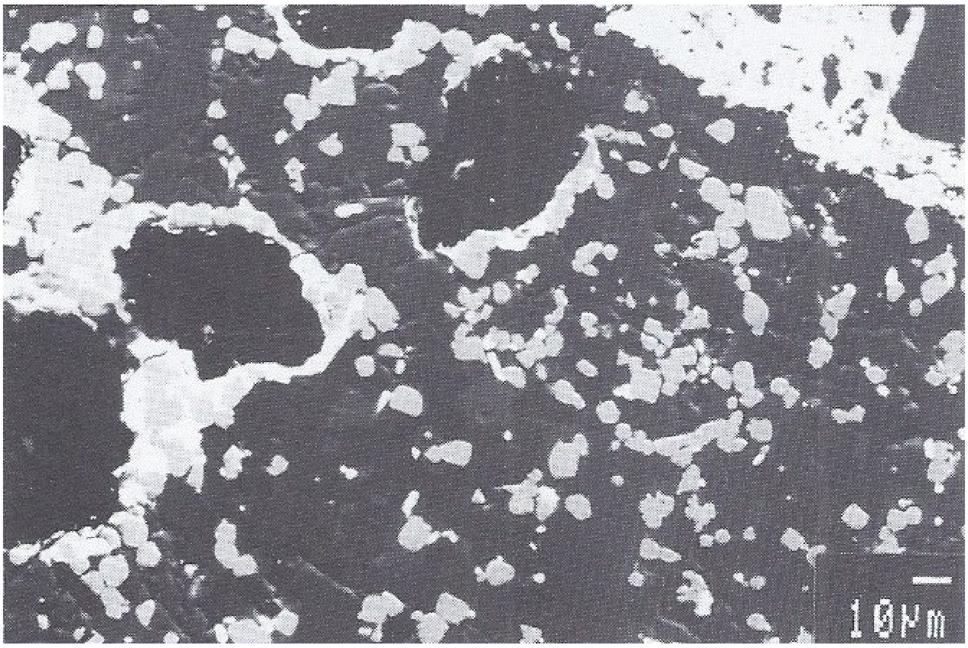

Fig. 2 Detail of low-zinc area with high-zinc matrix copper right. Common grains of $ZnAl_2O_4$ spinel, mid-grey occurs throughout, and are concentrated with Zn2Si04 (white) around pores (black) on the left and upper centre of photomicrograph. The low-zinc matrix consists of a two-phase mixture of silica and a potassium aluminosilicate glass; these are both dark shades of grey and only just resolvable.

I C Freestone

1988