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Reduction processes in the formation of lustre glazed ceramics

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Abstract

An earthenware type reduction lustre glaze containing bismuth, cobalt, copper and lead has been fired in H_2/N_2 atmospheres to produce successful lustre effects on ceramic surfaces. The glazes produced at different stages of reduction have been studied using energy dispersive X-ray and X-ray photoelectron spectroscopy. Thermogravimetry has been used to study the kinetics of the hydrogen reduction process. The results have been interpreted in terms of diffusional models. It is suggested that hydrogen diffusion into the glaze at the reduction temperature is very rapid. The rate of formation of the metallic clusters which give the lustre effect may be dependent on the rate of diffusional loss of water from the solid phase. The metal clusters are formed at depths of more than 5 nm below the surface of the glaze.

Keywords: Volatilisation; Thermogravimetry; Reduction lustre

1. Introduction

Reduction lustre is a highly decorative ceramic glazing technique traditionally carried out in an unmuffled kiln using wood for both heating and for generating the reducing atmosphere. Some contemporary kilns use gas or electrical heating. In the former cases the reducing atmosphere is generated by the use of an over rich fuel/air mixture. Reduction is by the introduction of hydrocarbon gases in the latter.

Precise control over the temperature, atmosphere and time during the reduction process is essential for success and this is extremely difficult to achieve in traditional kilns. Gas and electric kilns allow greater control but may pose safety and environmental problems through the production of toxic waste gases.

Temperature programmed reduction (TPR) studies of catalysts and other materials [1] have utilised hydrogen gas (5%) in nitrogen (95%) as a safe reducing atmosphere that produces no noxious effluent gases. TPR studies show that the reactive oxides commonly used in lustre glaze formulations are reducible in this atmosphere at or below the temperatures (650–700°C) used in reduction lustre processes.

We have demonstrated the feasibility of using the H_2/N_2 mixture as the reducing atmosphere in electric kilns for glazing ceramics [2]. From a wide range of lustre glazes for in-glaze lustre processes and clay pastes for on-glaze lustre an in-glaze lustre formulation was chosen for detailed study aimed at elucidating

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the mechanism of the reduction process. In-glaze lustres comprise a uniform, homogeneous layer of glassy material fused onto a ceramic substrate. The glass provides an inert matrix in which mechanically and chemically stable particles, capable of interfering with visible light, can form.

2. The glaze and the process

The glaze chosen for study was an earthenware type with the unity (molecular) formula shown in Table 1. The glaze matures (i.e. fuses to an homogeneous glass) at 1000–1100°C. Reduction is possible over a wide temperature range but the most successful temperature in terms of control of the process for aesthetic purposes is in the region of 680°C. At this temperature the glaze could be made to produce a range of lustre effects depending on the time for which the reduction was allowed to proceed. The mature glaze formed under oxidising conditions was an opaque dark blue colour. The early stages of reduction were characterised by a silver-blue lustre. Later phases of the process gave deep purple colours which eventually turned to a fully reduced reflective metallic copper colour.

Of the ions in the glaze, those for which hydrogen reduction is thermodynamically feasible under standard conditions are Bi^{3+}, Co^{2+}, Cu^{2+} and Pb^{2+}. However, the reduction of Co^{2+} is significantly less feasible than for the other ions. Under the non-equilibrium conditions prevailing in the reduction process, with 0.05 atm maximum pressure of hydrogen and an unknown (possibly high locally) pressure of water vapour, the reduction of Co^{2+} may be regarded as particularly unfavourable.

Earlier studies of glazes containing such reducible ions have resulted in conflicting evidence as to the nature of the reduced species and the lustre effects. Kingery and Vandiver [3,4] found both Cu(0) and Cu(I) in a red coloured Chun glaze. Wakamatsu et al. [5] however found that metallic copper was virtually absent from a similar red glaze. Later studies by Wakamatsu et al. [6] showed that the red colours in such copper-containing glazes could be associated with Cu_2O or Cu depending on the firing conditions which combined oxidation, reduction and neutral atmospheres in different ways. The Chun type of glaze on which the above studies were based are high temperature products (about 1300°C) and reduction was by CO in N_2 so the results of these studies may not be entirely relevant to the formation of lower temperature lustres. More directly relevant are the findings of Gaprindashvili et al. [7] who studied the composition of gold-violet coloured lustres in an earthenware type glaze containing Bi^{3+} and Co^{2+}. The variation of oxygen concentration with depth below the surface indicated that the lustre effect was developed at a depth of 10 μm. The colours were attributed to the presence of Bi(0). Kingery [8] has also attributed lustre effects in earthenware glazes to colloidal metal particles precipitated in the top few micrometres below the surface of the glaze and visible in transmission electron photomicrographs. In the studies reported here we have used reaction kinetics, photo-electron and X-ray spectroscopy measurements to gain an insight into the nature of low temperature reduction lustres and the mechanisms by which they form.

3. Experimental methods and results

3.1. Thermogravimetry

The glaze materials were fritted under oxidising conditions. The frit was pulverised to less than 100 μm. Approximately 40 mg samples of the powdered glaze were subjected to a programmed reduction process in a Mettler 3000 TG system. The programme consisted of heating the sample at 20 K min^{-1} to the reduction temperature in flowing air, holding the

Table 1
The unity (molecular) formula of the reduction lustre glaze[a]

Pbo	Na_2O	K_2O	CaO	CuO	CoO	Al_2O_3	B_2O_3	Bi_2O_3	SiO_2
0.16	0.18	0.11	0.48	0.05	0.03	0.15	0.61	0.05	1.45

[a] The numerical values are the molar amounts of each constituent of the mature, oxidised form of the glaze.

temperature constant for 5 min then changing to a 5% H_2 in N_2 atmosphere whilst maintaining the constant temperature. The weight loss during the reduction process was recorded for 1.5 h. Runs (Fig. 1) were carried out with reduction temperatures of 550°C, 570°C, 590°C and 610°C. Blank runs, with no sample, showed that the buoyancy effect apparent before the isothermal part of the TG was absent after the gas change-over point.

After the gas change-over a delay of about 3 min is seen during which the sample weight remains sensibly constant in each case. Following this, the initial weight loss is very rapid. In the runs at 550°C, 570°C and 590°C the initial rate is virtually independent of temperature (rate of change of extent of reaction $4.8(\pm 0.5 \times 10^4\ s^{-1})$ whereas at 610°C the rate during this period is approximately half the value ($2.5 \pm 0.5 \times 10^4\ s^{-1}$) of that at the lower temperatures. This behaviour is believed to be due to the facile removal of product water from the finest particles in the solid reactant coupled with their tendency to sinter at the highest temperature. In each case the kinetics are decelleratory throughout and equilibrium would be reached only after a very long period. The equilibrium weight loss is estimated from extrapolation to be 1.2%. From the glaze formula the calculated weight losses for complete reduction of each reducible oxide are Bi_2O_3: 0.93%, CoO: 0.18%, CuO: 0.31%, PbO: 1.00%. It is likely that under the reduction conditions prevailing only the Bi_2O_3 and CuO are reduced. This is in accord with the observations of ceramic artists who note that PbO reduction, which results in a "greying" of the glaze, only occurs after prolonged reduction at higher temperatures [9]. The CoO reduction has already been noted as being thermodynamically unfavourable.

3.2. Energy dispersive X-ray analysis

A series of glaze samples was prepared for surface analysis by energy dispersive X-ray (EDX) in a scanning electron microscope. The samples were prepared on 150 mm square white earthenware tile substrates. Each tile was glazed and fired in a 2 l muffle kiln under oxidising conditions at 1060°C with a 1 h soak period. After cooling to the required reduction temperature the glaze was reduced in flowing 5% H_2 in N_2 for 15 min in the muffle. Following reduction the samples were cooled in a nitrogen atmosphere. The reduction temperatures used ranged from 580°C to 1000°C. The sample produced at 580°C was shiny but non-lustrous, those from 630°C to 780°C had increasingly lustrous appearance, and at 830°C and above the glaze became cloudy, dull, non-lustrous.

Each sample was placed in the electron microscope (Link 850 model) and subjected to surface analysis by EDX using ×30 magnification and 15 kV accelerating potential. These conditions ensured that a representative area was examined to a significant depth of several micrometres. Elements down to Na could be detected. The EDX method did not show the presence of Co. Bi and Pb were detected but not measured because their peaks could not be resolved. Of the elements measured, most (Al, K, Ca, Ti, Fe) were indicated to be present in all the samples in relatively constant proportions. However the Si and Cu varied in proportion considerably from sample to sample and showed an inverse relationship (Fig. 2).

Changes in the surface concentration of copper may be caused by volatilisation, a phenomenon often noted in lustre glazing through colourisation of flames in exit flues of kilns [10]. Volatilisation would be expected to result in the observed behaviour, i.e. an increase in relative surface concentration by diffusion from the glaze interior and then a decline as the overall concentration falls. At the temperatures used in the present TG and X-ray photoelectron spectroscopy (XPS) studies (in the region of 600°C) no significant metal volatilisation would be expected, so the concentration changes which were observed by XPS (q.v.) should be ascribed to other causes.

3.3. X-ray photoelectron spectroscopy

A number of earthenware tiles and vases glazed with the standard glaze were fired and reduced under a flowing H_2/N_2 gas stream in a 9 l electric kiln primarily to assess the aesthetic qualities of the products. These tiles and vases showed variations in the degree of reduction due to gas flow patterns, temperature gradients and convection currents in the kiln. A typical tile showing such variations was cut to give three pieces which respectively had the appearance of being unreduced (dark blue non-lustrous), partially reduced (silver-blue lustre) and fully reduced (reflective metallic copper). Each of these was subjected to XPS

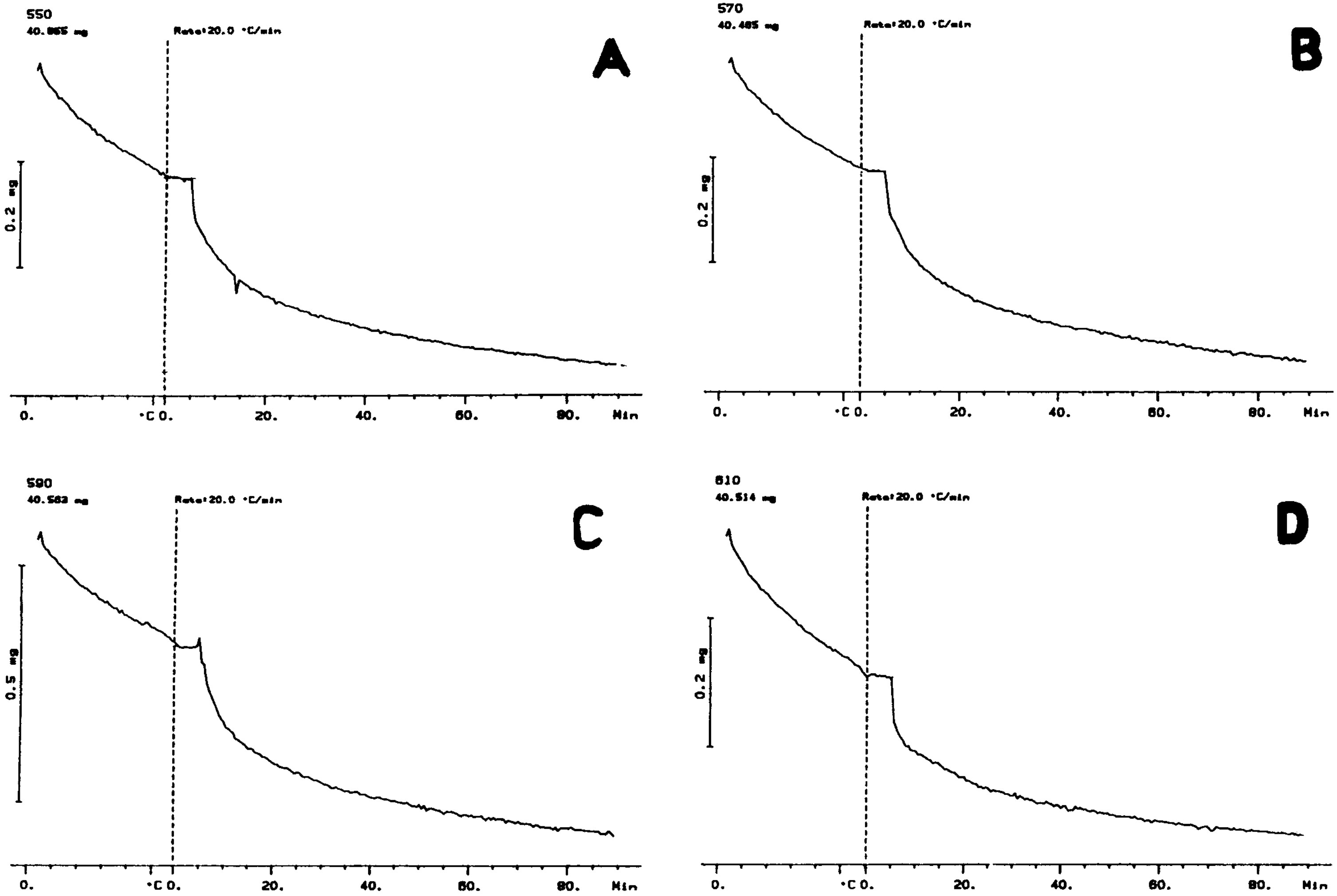

Fig. 1. Programmed thermogravimetry of the glaze. In each case the heating was at 20 K $\min^{-1}$ to the isothermal temperature. The reducing gas was introduced, and the isothermal conditions start, at the point shown by the dashed line. Sample weights and temperatures are (A) 40.855 mg, 550°C; (B) 40.485 mg, 570°C; (C) 40.583 mg, 590°C; (D) 40.514 mg, 610°C.

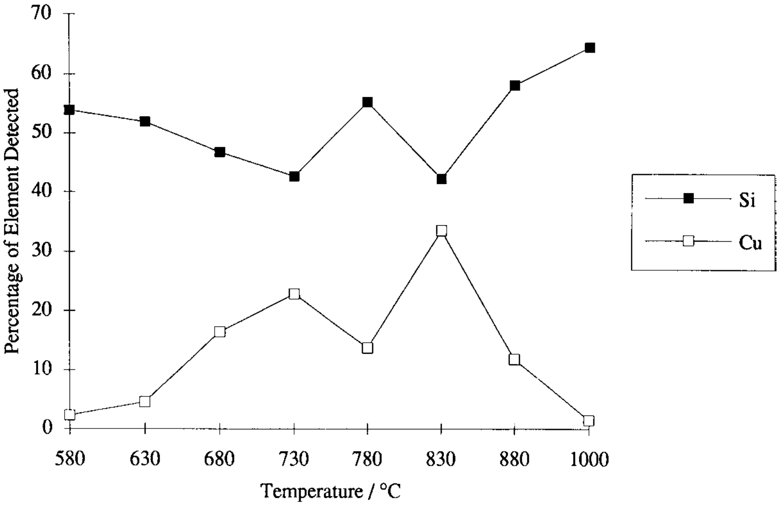

Fig. 2. EDX measurements of Cu and Si in glazes reduced at different temperatures.

analysis with the aim of obtaining mainly qualitative information on the valence states of the reducible elements in the glaze surface. A vacuum generators escalab Mk II spectrometer was used with AlKα radiation (energy 1486.6 eV) at 10 kV, 40 mA and pass (analyser) energy 50 V. The sample was held normal to the detector. Tilting the sample caused severe deterioration of the signal quality. Repeat scanning and signal averaging was used over the ranges of interest. These regions included an initial wide scan of binding energies from 0 to 1200 eV; then the carbon 1s, oxygen 1s, copper Auger and copper 2p regions. The samples were highly charged (10–15 eV), the charge being assessed by reference to the position of the Carbon 1s peak. Charge compensation was not used. The wide scan spectrum covering the 0–1200 eV binding energy range for the partially reduced glaze showed (Fig. 3) significant peaks for copper but other ions of interest also relatively abundant in the glaze gave much lower intensity peaks. The peaks of interest were of very low intensity in the oxidised and fully reduced glazes. Significant diagnostic information could not be obtained from the copper Auger peaks in the partially reduced glaze because there are no comparable peaks in the other two spectra. The raw data for the copper photoelectron peaks at 920–970 eV are shown on expanded scale for all three samples in Fig. 4. The three curves are presented at comparable sensitivities from which it can be seen that the unreduced glaze and the fully reduced glaze appear to have very much lower surface concentrations of copper than does the partially reduced material. An important qualitative difference between the samples is that the partially reduced sample shows satellite peaks indicative of Cu^{2+}. The ratio of the satellite to the Cu 2p3/2 peak is approximately 0.4 : 1, confirming that this sample is partially reduced (pure Cu^{2+} gives a ratio of 0.6 : 1). The unreduced glaze also shows satellites, though these appear less well developed; but there can be no doubt that the copper, being prepared under oxidising conditions, would be present as Cu^{2+}. The fully reduced, copper coloured specimen has Cu PES peaks but these are of extremely low intensity. This is thought due to the metallic particles being formed at depths greater than the few nanometres which is the escape depth for photoelectrons (discussed later).

4. Discussion

4.1. A proposed reaction mechanism

Glazed tiles reduced in a variety of ways have previously been viewed by SEM in cross-section [2,8]. The results showed that the lustre layers are confined to the top few microns of the glaze surface. The observations suggest that the reduction reaction

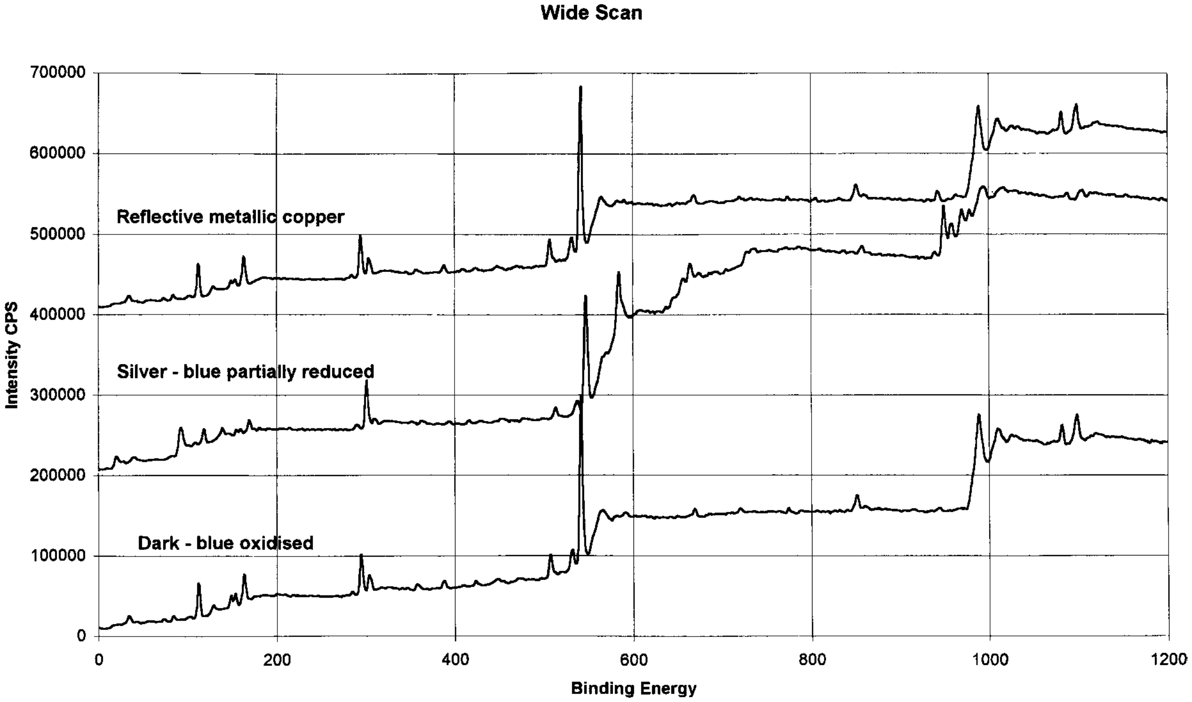

Fig. 3. Wide scan XPS spectra of the glazes in oxidised, partially reduced and fully reduced states.

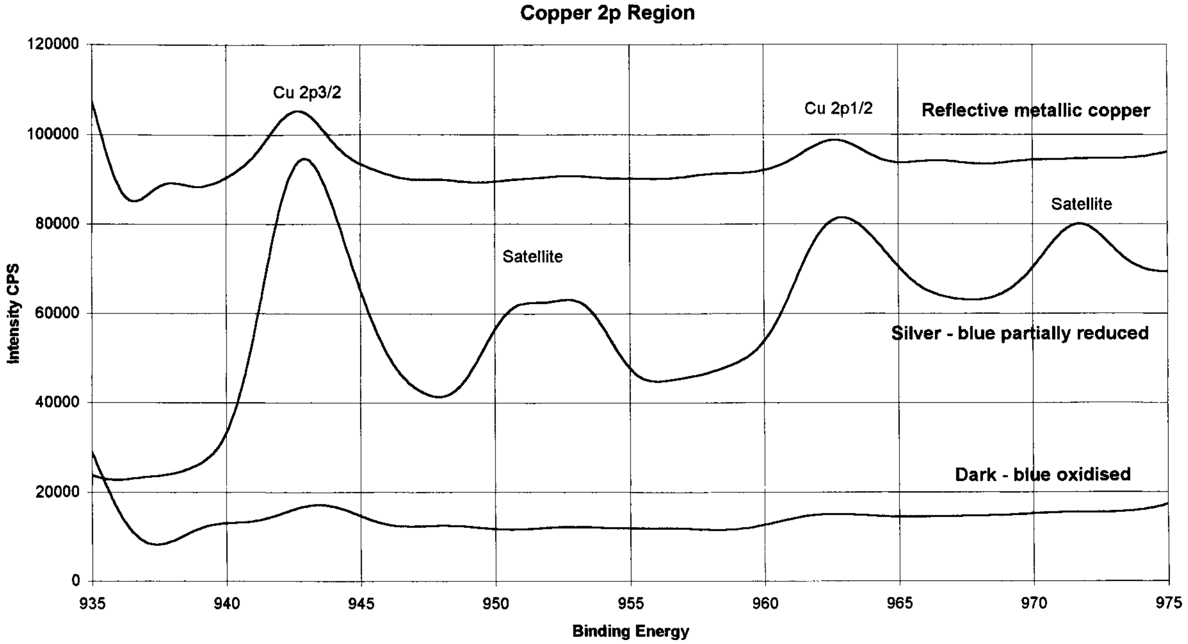

Fig. 4. Copper PES peaks in the XPS spectra of glazes in oxidised, partially reduced and fully reduced states.

may have the characteristics of a surface or topochemical process rather than an homogeneous one. The process of formation of reduction lustre may have at least the following basic mechanistic steps:

(a) Diffusion of H_2 gas into the glaze.
(b) Chemical reaction within the matrix of the glaze.
(c) Diffusion of metal atoms to form metal clusters within the glaze.
(d) Diffusion of metal ions through the glaze towards depletion zones.
(e) Diffusion of water from the reaction zone to the glaze surface.

In (a) the reducing gas can be assumed to flow at a reasonable replenishment rate over the glaze surface so that the hydrogen concentration in the gas phase at the surface remains sensibly constant.

In (b) the reaction may take place in a single stage (e.g. Bi(III) to Bi(0)) or in more than one stage (e.g. Cu(II) to Cu(I) to Cu(0)).

In (c) the clustering produces particles of metal large enough to cause interference with visible radiation and ultimately metallic reflection.

The rate of step (e) is measured by the TG experiments but this is not necessarily the rate determining step in the overall process.

4.2. *Mathematical models for the proposed mechanistic steps*

The TG data show a linear relationship between weight loss and the square root of time (Fig. 5) over the first 50% of reaction. The calculated rate constants at the three lower temperatures used obeyed the Arrhenius equation (Fig. 6) showing that the reaction mechanism was probably independent of temperature over this range. The activation energy is calculated to be 86 kJ mol^{-1}.

The later 50% of the TG curves were found to obey a first order decay law but the associated rate constants obtained did not obey the Arrhenius equation. This is likely to be due to sintering. It was noted that at the highest temperature the frit was markedly sintered at the end of the TG reduction period. Given the changing surface area of the reactant frit the obedience to the first order decay law may be regarded as a purely empirical phenomenon with no simple mechanistic explanation. Sintering would also be the reason for the run at 610°C failing to conform to the Arrhenius equation in the earlier stages of reaction. It is possible that the calculated activation energy is suppressed for the same reason even at lower temperatures though there was no visual evidence of this and the Arrhenius plot is quite linear over the lower temperature range.

The mass transfer proportional to $(\text{time})^{0.5}$ rate law is a solution to Fick's law for diffusion at a constant area interface of semi-infinite media [11]. This rate law, along with the relatively small activation energy, suggests a diffusional model to be appropriate for the system here considered over the first 50% of reaction at the lower temperatures. The proposed mechanism has four diffusional steps. Of these (a), (d) and (e) would obey the square root time law. In step (c) the clustering of metal atoms would be similar to precipitation from solution. It is shown later that this step would not obey the square root time law in the TG experiments.

4.3. *Rates of diffusion at the reaction interface*

Given that the reaction is diffusion controlled it is possible to refine the proposed model by the calculation of theoretical rates for comparison with the experimental observations.

A problem often found in dealing with diffusion problems is the lack of availability of the diffusion coefficient, D, for the system of interest. A theoretical model for the estimation of D values for gases in glasses has been proposed [12]. The model can yield values of D close to experimental values but the model requires a knowledge of the probability density function of the diffusion sites and a reliable experimental diffusion coefficient for at least one gas for normalisation. The value of the model has been that it demonstrates that diffusion rates in glasses are largely governed by the size of the diffusing species because this places restrictions on the volume and number of jump sites. An increase of 10 pm in the radius of an atom of about 150 pm radius may reduce the diffusion coefficient by over 50%. Published experimental solubility and diffusion data [13] for atoms and neutral molecules in glasses accord with this.

The use of estimated values of D allows order of magnitude calculations to be performed relevant to the various diffusion steps in the proposed mechanism.

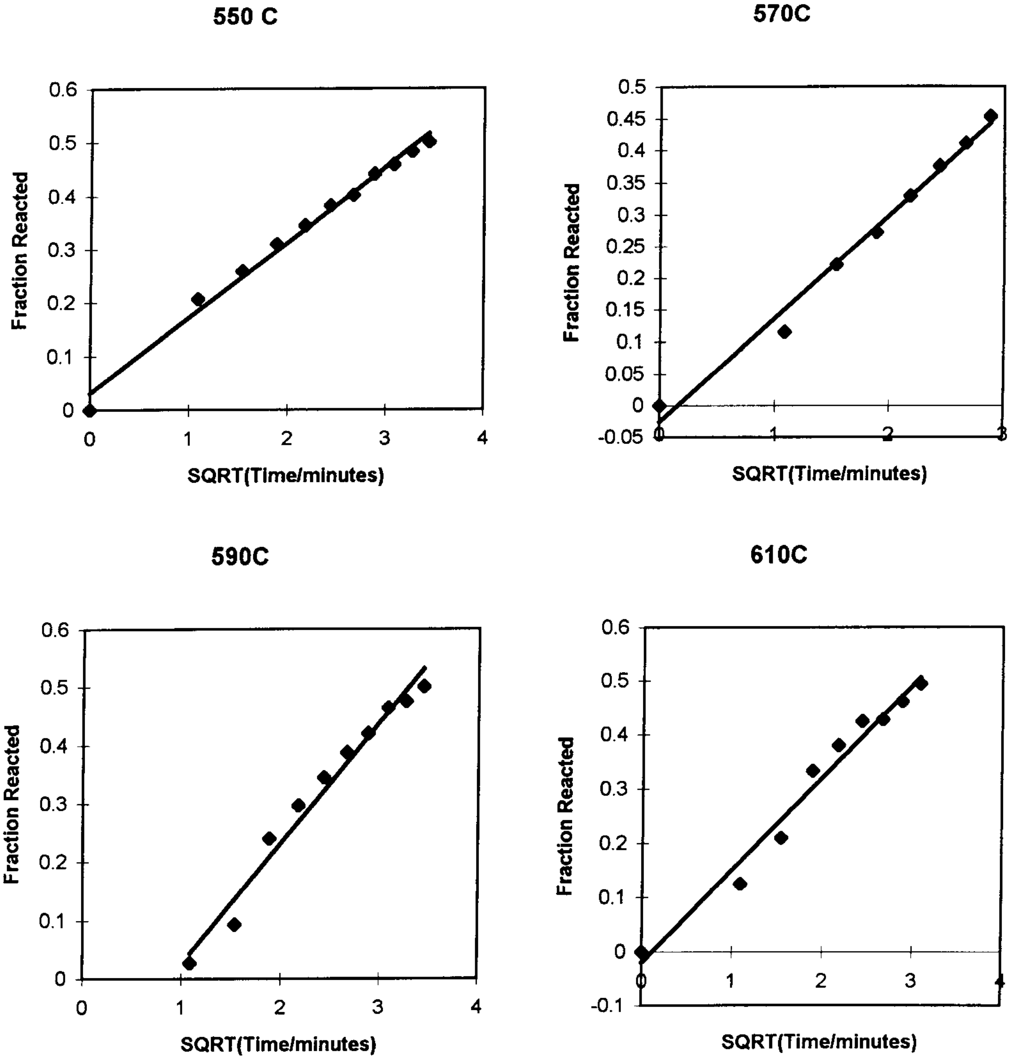

Fig. 5. Fraction reacted vs sqrt(time) over first 50% reaction in the isothermal TG.

For the lustre glazing system the diffusing species of interest are the hydrogen gas, the reducible ions and the product metal atoms and water. Table 2 shows published data which can be used to effect these approximate calculations for the gases involved.

The way the concentration of hydrogen, as a percentage of that present at the solid/gas interface, varies with time at specific depths in the initially hydrogen-free solid can be calculated using Fick's second law. For an infinite system with constant surface

Table 2
Diffusion coefficients for gases in glass [12]

Diffusing species	Type of glass	Temperature (°C)	D (m^2 s^{-1})
Hydrogen	SiO_2 glass (I.R. Vitreosil)	700	2.7×10^{-11}
Water vapour	SiO_2 glass (I.R. Vitreosil)	800 (approximate)	2.0×10^{-14} (approximate)

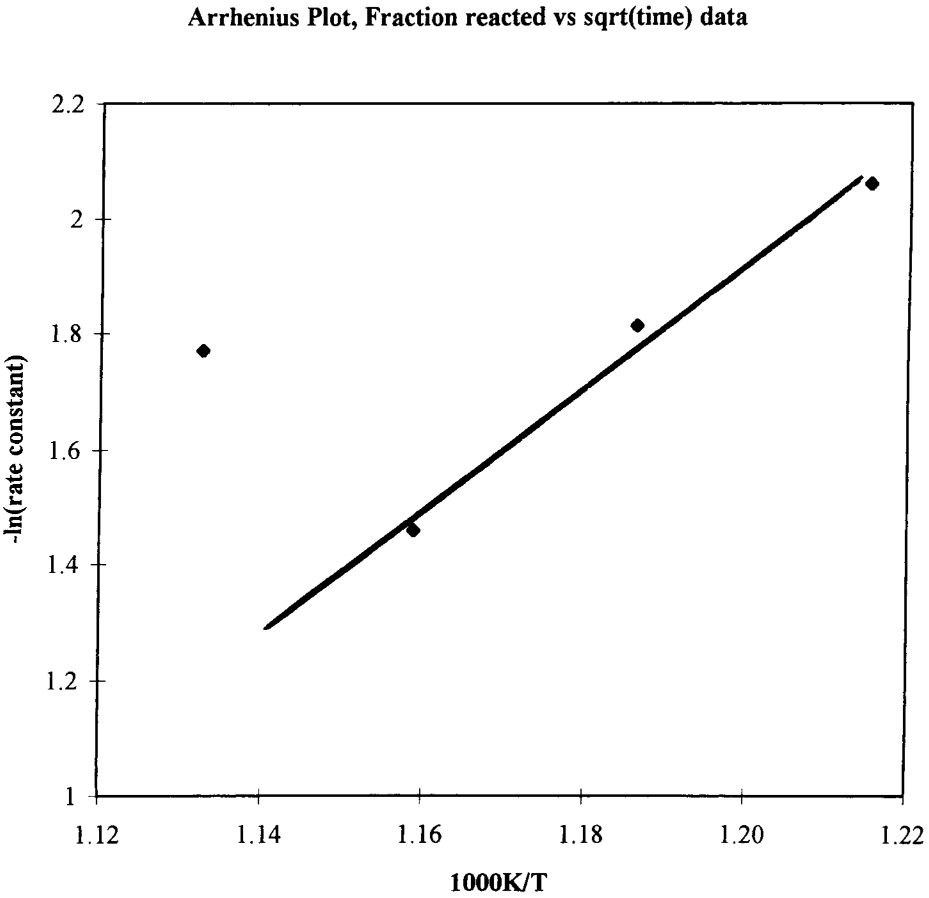
Arrhenius Plot, Fraction reacted vs sqrt(time) data

Fig. 6. Arrhenius plot, fraction reacted vs sqrt(time) data.

concentration Fick's law gives [11]:

$$C_{t,x}/C_s = 1-\mathrm{erf}[x(2(Dt)^{0.5})], \quad (1)$$

where $C_{t,x}$ is the concentration of diffusing species at time t and depth x, C_s, the constant surface concentration of the diffusing species D, the diffusion coefficient is assumed constant at constant temperature.

Calculations using Eq. (1) confirm the ease of hydrogen diffusion (with $D = 2.7 \times 10^{-11}$ m^2 s^{-1}) since it is seen capable of achieving 90% saturation at a depth of 10 microns in less than 2 min.

By contrast, reduced species in this layer, particularly bismuth, would diffuse more slowly due to their larger size. H_2, Bi^0 and Cu^0 have atomic radii of approximately 125, 146 and 128 pm respectively [14].

The diffusion of metal ions is not comparable to that of neutral species. Zn^{2+}, Cd^{2+} and Ca^{2+} in a silica glass at 800°C were found to have $D = 1.3 \times 10^{-17}$, 3.5×10^{-18} and 1.8×10^{-18} m^2 s^{-1} respectively [13] suggesting that ionic species of sizes comparable to Cu^{2+} and Bi^{3+} diffuse extremely slowly in glasses. Thus, after reduction, the ions would not be replaced at any significant rate by diffusion from adjacent areas in the glass.

The escape of water from the reaction zone, given the thousandfold smaller D value than that of hydrogen, would be much slower than the rate of diffusion of hydrogen into the glaze and would be the rate determining step in the TG experiments.

It can be concluded that the reduction reaction takes place in an homogeneous solid solution of metal ions and hydrogen.

4.4. *Rate of precipitation of metal particles*

The formation of the lustre, as distinct from the rate of reduction, might be controlled by the rate of loss of water from the glaze or it might be governed by the rate of precipitation of metal particles in the glaze matrix.

A value for the diffusion coefficient of the metal atoms produced in the reduction process is not available. However, that for argon, (atomic radius 191 pm [14]) is calculated as being approximately one fifth that of hydrogen molecules under the same conditions [12]. From Table 2, taking one fifth of the D value for hydrogen would give, for argon, $D = 0.5 \times 10^{-11}$ m^2 s^{-1}. Independent experimental measurements of argon diffusion at 400–900°C gave, in silica [15] $D = 3 \times 10^{-10}$ m^2 s^{-1} and in a silica glass [16] $D = 9 \times 10^{-10}$ m^2 s^{-1}. Bi^0 and Cu^0, being significantly smaller, probably diffuse more rapidly. For an order of magnitude calculation the lowest of the three values for argon might be taken as representing the slowest possible case for the metals.

Solution of Fick's second law for the initial stages of precipitation of particles at the centre of spherical shells approximating to space filling polyhedra is [12]

$$C/C_0 = \exp(t/\tau)^{3/2}, \tag{2}$$

where C is the average concentration in the medium at time t, C_0, the initial concentration in the solution, τ, the relaxation time.

The relaxation time is approximately the time taken to reach 0.67 fraction reacted. In this case τ is given by

$$\tau = (r^2/2D)(C_p/C_0)^{1/3}, \tag{3}$$

where C_p is the concentration of solute in the precipitate, τ is constant at constant temperature, r, the radius of the equivalent spherical shell.

In terms of the TG experiments, in Eq. (2)

$$C/C_0 = [M]_t/[M]_0 = 1-f, \tag{4}$$

where f is the fraction of metal ion, M, (copper + bismuth) reacted, or the fractional weight loss from the TG curve.

Then, from Eqs. (2) and (4)

$$\ln(1-f) = t^{3/2} + \text{constant}. \tag{5}$$

Thus, if formation of clusters were rate determining, a linear relationship between $\ln(1-f)$ and $t^{3/2}$ would be observed in the TG. This is not the case.

It is nevertheless worth considering the time scales for the formation of colloidal metal particles by the precipitation process, assuming the absence of complications such as inhibited nucleation, Bi–Cu phase equilibria and effects of particle shape.

From the glaze recipe the mole fraction composition of the metal particles would be 1/3 Cu : 2/3Bi. A particle of this composition and of 500 nm radius (i.e. capable of interfering with visible radiation) would weigh 5×10^{-12} g. Formation of such a particle would completely deplete the Cu^{2+} and Bi^{3+} content of a spherical shell having a radius of 1.8 μm. (Using 2.25 g cm^{-3} as the density of the glass and 9.5 g cm^{-3} as the density of the metal.)

For a precipitation cell of this size, using Eq. (3) with $C_p/C_0 = 45$ (from the glaze formula and the density data) and, $D = 0.5 \times 10^{-11}$ m^2 s^{-1} (diffusion of metal atoms) the relaxation time would be approximately 2 s. Thus the precipitation rate is unlikely to govern the rate of formation of the lustre effect. The metal particles would form, from an homogeneous medium where copper ion replacement into the precipitation cell was negligible, at about 1.8 μm depth below the surface. This is below the range of detection by XPS. Any particles growing from nuclei closer to the surface would not reach the required size on this simple model. This explains why, in the partially reduced glaze Cu is detected by XPS but in the fully reduced glaze the copper does not yield a strong XPS peak; the particles are at too great a depth for detection by this technique.

5. Conclusions

The experimental studies described, along with approximate calculations of the rates of diffusion controlled processes are consistent with a reduction lustre formation mechanism in which:

1. the glaze is rapidly saturated with hydrogen from the gas phase;
2. metal particles with lustre properties initially can form quickly at depths (less than 5 nm) where they are detectable by XPS;

3. metal ion depletion at the glaze surface caused by the reduction process is only slowly made good by diffusion from the glaze interior;
4. continued reduction results in further growth of metal particles which, when demonstrating full metallic reflection properties are at a depth below the surface beyond the detection range for XPS;
5. the rate of formation of the lustre is controlled by the slow rate of diffusion of water through the glaze from the reaction zone to the evaporative surface.

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