Control of oxidation state of copper in flame deposited films

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ARTICLE INFO

ABSTRACT

The deposition of thin copper based films onto carbon steel surface is described, using premixed flames with different oxygen/methane ratios doped with aqueous copper nitrate as precursor. We investigated the chemical properties of the copper as a function of oxygen/methane ratio. Using fuel rich flames (equivalence ratio 0.665), the deposited copper film was entirely metallic. When the equivalence ratio was increased to 0.850 or greater the copper film contained predominantly Cu^{2+}. Furthermore, the flame can be used for post deposition modification, as demonstrated by reduction of Cu^{2+} containing films to Cu metal. All the films were characterised by X-ray diffraction, Raman and scanning electron microscopy (SEM). A rotating sample holder was employed to avoid over heating of the sample and the critical variables such as sample height in the flame and deposition time were optimised. Deposition for 20 min, which translated to a total residence time in the flame of approx. 76 s, produces metallic copper films of thickness 169 ± 18 nm as determined by anodic stripping and SEM. The microstructure of the metallic films was clearly composed of fused copper spheres of 100–150 nm, which are probably formed in the flame and subsequently deposited on the surface with good adhesion.

1. Introduction

Deposition of thin coatings on surfaces is an immensely important process to meet the demands for synthesis of functional and smart materials. Normally coatings are deposited to extend the working life of a particular component (e.g. anti-wear properties) or change the surface functionality (e.g. catalytic coatings). One aspect of materials synthesis is to focus on making the deposition process quick, efficient and environmentally sustainable. Existing deposition methods are very varied and in general the coating method is tuned to a particular application and coating material or property. Here we show flame based methods for the deposition of copper based thin films with control of oxidation state.

The deposition of metals or metal oxides is extremely important for many commercial applications ranging from so called intelligent coatings which respond to the environment [1,2] to structured coatings on a nanometre scale for antibiotic properties [3], to name but a few. Very often metal based coatings are deposited on a surface from a very well chosen precursor, to create a precisely tuned coating which may be composed of two or more metal based species. The deposition conditions are generally unchanged as they control the integrity of the coating such as uniformity and micro or nanostructure. Chemical vapour deposition is an excellent example of this methodology. The breadth of precursors which may be delivered concurrently provide a wide variety of surface coatings, whilst the basic physical conditions such as substrate temperature and precursor delivery rate are highly controlled. The precursor normally undergoes a chemical reaction and breakdown at a hot substrate (~400 °C) resulting in the formation of a film [4].

Here we present a technique which combines the versatility of flame based deposition with control of oxidation state of the metal deposit. Flame based deposition techniques are divided in two categories; flame spraying and flame pyrolysis. Flame spraying can be used to deposit metallic particles and involves the physical blasting of particles with the desired material onto a surface. Particles are normally in the range of tens of micrometres [5], although it is possible to use nanoparticles and delivered from an aerosol [6]. Flame spraying produces very uniform films with controllable thickness and physical, mechanical properties. The chemical make-up of films produced in this way is not very controllable, often the fuel is Kerosene mixed with oxygen and the conditions are optimised for optimum film growth [7]. Flame based pyrolysis or vapour based reaction followed by deposition, also called flame chemical deposition represents a very popular method of deposition. This method produces very uniform films with good cope of for scale-up [8]. More relevant to this study, Sheel et al. [9] deposited copper oxides using copper nitrate precursor in an oxygen rich propane burner. They showed that the surface morphology can be changed by modification of the substrate (glass) temperature producing CuO isolated particles, which have biocide properties.

There are many examples in the literature of flame synthesis of nanoparticles. The size, morphology and composition can very

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precisely be controlled and production can be easily scalable [8,10,11]. Many catalytic materials have been demonstrated in the form of oxides and oxides decorated with noble metals. Mädler et al. [12] showed that it was possible to synthesise gold decorated TiO_2 or SiO_2 by concurrent delivery of pyrolysis precursors to produce TiO_2 or SiO_2 and gold nanoparticles in a methane oxygen flame and collected on filters.

In the past we have utilised flames as a medium for electrochemical measurements [13–16], here we use a very simple model system of copper deposited on a steel substrate. By adjusting the ratio of oxygen and methane the oxidation state of copper can be controlled very precisely. Metallic copper layers or Cu^{2+} may be deposited depending on the flame mixture using a copper nitrate salt in aqueous solution.

2. Experimental details

2.1. Materials and methods

Individually controlled digital mass flow controllers (5850S, Brooks, USA, with IGI control interface, UK) where used to control all gas flows from methane (99.995%), oxygen (99.9+%) and nitrogen (99.99%) from compressed gas cylinders supplied by BOC. Before reaching the burner the gases were thoroughly mixed in a chamber which included a blow-out panel to protect against flash back; *NB. Pre-mixed methane and oxygen gases are explosive and hence adequate safety precautions were taken*. The ratio of methane and oxygen was changed to obtain three stable flames with different mixtures referred to herewith as Flames 1, 2 and 3 as shown in Table 1. The total flow rate of nitrogen stream was constant at 650 ml min^{-1} and was used to transport the precursor to the burner.

Aqueous solutions of copper nitrate (Sigma Aldrich) was prepared using deionised water (Millipore Milli-Q® gradient, <0.05 S cm^{-2}). The solutions were introduced into the gas stream in the form of an aerosol created from a modified ultrasonic atomiser (Index Ltd. UK). In all this work a solution (10–20 cm^3) of copper nitrate (0.5 mol dm^{-3}) was transferred to a modified round-bottomed flask placed in the ultrasonic atomiser through a side injection port by syringe during an experiment. The aerosol produced in the round bottomed flask was carried by the nitrogen stream to the mixing chamber. On exit from the burner the aerosol was essentially dry with small crystals of copper nitrate entering the flame.

The burner was of a Meker design, described in reference [17], with 19 holes each of 0.5 mm diameter, arranged in a near hexagonal array {3, 4, 5, 4, 3}. This forms a laminar flame with a diameter of approx. 8 mm and a height of 100 mm. The brass top-plate was cleaned by skimming the top surface, and the holes where carefully cleaned using a 0.5 mm diameter drill after each set of experiments. The burner was mounted vertically on an earthed aluminium table. The gas lines were dried by passing nitrogen at 200 ml min^{-1} for at least 2 h prior to an experiment.

The samples used in all this work were carbon steel (98% Fe, 1.7% Mn and 0.3% Cr) of rectangular shape, (cuboids: $2 \times 1 \times 0.6$ cm). All samples were cut from the same piece of carbon steel pipe, to maintain high sample uniformity. After being machined polished and

Table 1
Showing the three flame systems used in this work with their corresponding oxygen/methane ratio, flow rates and adiabatic flame temperature.

Flame system	Equivalence ratio[a]	Flow rates, $O_2/CH_4/N_2$ in ml min^{-1}	Adiabatic flame temperature/K
Flame 1	0.665	600/450/650	2720
Flame 2	0.850	510/300/650	2767
Flame 3	1.165	700/300/650	2788

[a] Equivalence ratio is calculated using $(O_2/CH_4)/\lambda$, where λ is the ratio of (O_2/CH_4) at stoichiometric flame = 2.

sonicated in acetone, the samples were mounted onto the rotating arm 7.0 cm long, Fig. 1. The sample was passed through the flame at a pre-defined height above the burner at a rotation rate of 5.0 Hz. This ensured that the sample did not heat up, in fact the sample temperature was not higher than 100 °C, while the temperature of the hottest part of the flame given by the adiabatic flame temperature was 2720 K, the surface temperature of a steel sample placed in the flame as measured by thermal imaging camera (800–3000 K, mod. M9100, Mikron instrument Company Inc., USA) was 1350 °C. High speed camera (Phantom MIRO 4 monochrome) was used to estimate the transit time of the sample (substrate) spent in the flame during each experiment. It was estimated that for the duration of experiments of 20 min, the sample (substrate) spends effectively 78 s in the flame, (6.5% of the total time).

2.2. Characterisation techniques

The surface morphology, chemical composition/structure and film thickness of the flame deposited samples were analysed by the means of SEM and Energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy, X-ray diffraction (XRD) techniques and striping voltammetry, respectively. SEM images were obtained by using either Hitachi (S-3400N model) or JEOL (field emission 6005) instruments, while a Philips SEM instrument (XL30ESEM with Oxford Instruments Inca WD software), was used for elemental analysis. The accelerating voltage of 5 keV was applied in all analyses performed in wave dispersive mode, using Cu Lα, Fe Lα and O Kα lines. Raman spectroscopy was used for identification of deposited species on the substrate surface. The 514 cm^{-1} line of an Ar$^+$ laser was used as excitation source, (Renishaw inVia Raman Microscope).

X-ray diffraction (XRD) patterns were recorded on Bruker AXS, D4 ENDEAVOR instrument with CuKα radiation ($\lambda_1 = 1.54056$ Å and $\lambda_2 = 1.54430$ Å) in reflection mode with 2θ between 5 and 85°, the time of 2.0 s/step, and increment 0.05°. Striping voltammetry was used for the estimation of total elemental copper deposited on the steel samples. An Ecochimie (μAutolab, Windsor Scientific) potentiostat supported by GPES software was used to perform stripping voltammetry of a defined surface area of the sample. An Ag/AgCl was used as reference electrode and platinum wire was used as counter electrode. The potential was scanned from -0.8 to -0.3 V vs. Ag/AgCl at a scan rate of 0.1 V s^{-1}. The charge of the oxidation peak was determined by integration, the copper density was 8.94 g cm^{-3}.

3. Results and discussion

In this work we used copper nitrate solution atomised in the pre-mixed gases at room temperature. The gas stream was ignited which produced a stable flame containing the doped copper salt. The delivery efficiency was low. During a 20 minute experiment approximately 4 cm^3 of solution was atomised but only a small fraction (~5%) of copper salts was delivered to the burner. The surface coating was characterised as a function of deposition time, height of the sample above the burner top and flame oxidant/fuel ratio. A blank experiment was performed where a sample was placed in the flame for 20 min, rotated at 5 Hz at 1.2 cm above the burner top, with aqueous solution containing no copper nitrate. The sample was analysed using Raman and EDX and showed that there was little or no change to the surface compared to a fresh untreated sample, results not shown. EDX analysis of this sample confirmed that metal composition in atomic percentages was, $97 \pm 2\%$, $1.5 \pm 0.2\%$ and $0.4 \pm 0.03\%$ of iron, manganese and chromium, respectively, reflecting the starting composition very closely.

In the first set of experiments, Flame 1 doped with cooper nitrate solution, the height of the rotating sample above the burner top was varied between 0.6 cm and 5.0 cm. The concentration of solution
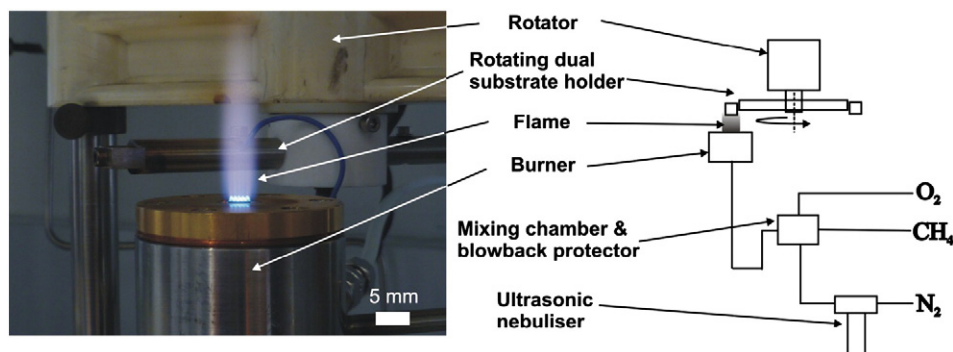
Fig. 1. Photograph of flame and the sample holder which rotates and transiently positions the sample in the flame. Right; schematic of the flame deposition apparatus, showing the flow system including the mixing chamber and nebuliser.

(0.5M), rotating speed of 5.0 Hz and the time (20min.) of these experiments were all kept constant.

It was observed that the surfaces of the samples positioned at 0.6 and 1.2 cm were smooth, evenly covered with the shiny reddish metallic deposit, indicative of elemental copper. In contrast, the matt grey surfaces were observed in samples kept at 3 and 5 cm. The evolution of surface morphology and the ratio of elements present in the thin film deposited on the steel substrate were estimated by the SEM/EDX analyses. SEM images of all the samples alongside including a fresh unmodified sample and the percentage copper measured by EDX are shown in Fig. 2.

As can be seen from Fig. 2b and c, the change of a height of the substrate from 0.6 to 1.2 cm did not result in a noticeable change of the film morphology and in the amount of elemental copper deposited. However, further increase in height of the substrate from the burner top to 3.0 cm and 5.0 cm, showed a significant effect on the surface morphology of the deposit. SEM images of the substrate held at 3 cm and 5 cm show that the surfaces of these samples were covered with irregular, sharp grains. EDX analysis of these two samples showed that they contain much less copper and consequently, more oxygen and iron. The appearance of the iron oxides suggests that the coverage of copper was poor at these heights. Indeed EDX

analysis showed a decrease in deposited copper, from 67 at.% at 0.6 cm, down to ca. 6.3 at.% at 5.0 cm. This was likely due to coalescence and further oxidation due to oxygen entrainment, of copper particles in the flame as they travel up the flame and not adhering to the substrate very well. Furthermore, the surface morphology of these samples changed from smooth, equally distributed layers of elemental copper to the randomly distributed, isolated, copper/iron oxide grains. The trend of these changes is graphically illustrated in Fig. 2f. In order to reduce excess sample heating and avoid entrainment of ambient oxygen (which would change the fuel oxidant ratio), it was concluded that the optimal height of substrate for deposition of elemental copper in reducing flames is 1.2 cm. Therefore, all further investigations of copper deposition were carried out on the samples (substrates), held at 1.2 cm above the burner top.

The deposition time was varied to see how the thickness and surface morphology changes with time. In these set of experiments the deposition time was varied between 5 and 20 min, while the height of the sample (substrate) above the burner was kept constant at 1.2 cm. As stated earlier, the rotation speed of the sample and the flame were also kept the same. For all the experiments, the resulting surface coating was very uniform and adherent; it was not possible to remove the coating with adhesive tape. EDX analysis was carried out
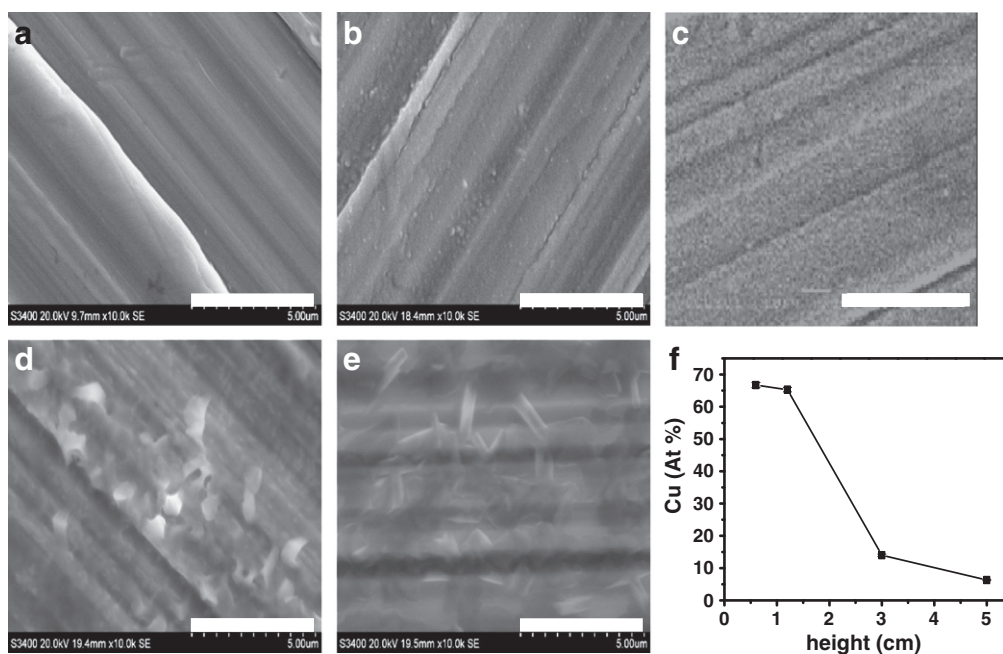
Fig. 2. SEM images (10 k magnification) as a function of height of the substrate in reducing flame; a) flame without Cu (blank sample) at 1.2 cm; flame with Cu(NO₃) added with sample held at 0.6, 1.2, 3.0 and 5 cm above the burner top b), c), d) and e) respectively. f) shows a plot of atomic percentages (obtained from EDX) of copper against the height of the sample. The surface morphology was dominated by the set of parallel machining lines are from the sample preparation. The scale bars on all the SEMs represent 5 μm.
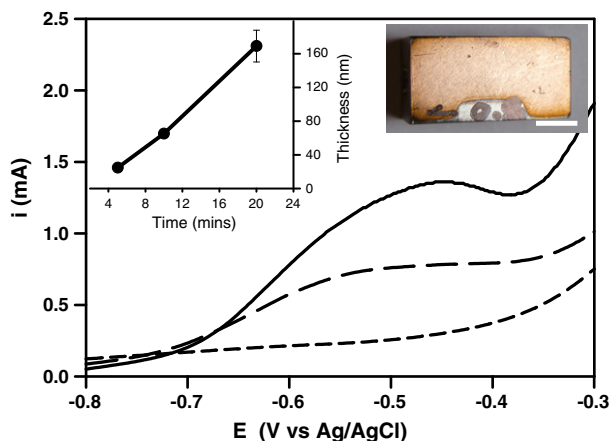
Fig. 3. Anodic stripping voltammograms of the samples treated in reducing flames for 5 (– – –), 10 (– – –) and 20 (——) minutes. Flame 1, 0.5 M copper nitrate with a rotation rate of 5 Hz. Left inset is the plot of copper film thickness against deposition time. Right inset showing photograph of copper deposit on carbon steel after 20 min deposition time, scale bar represents 2.5 mm.

at 5 keV and the percentage of copper was clearly increasing as the deposition time increased (37 at.% and 67 at.% after 10 and 20 min respectively).

The thickness of the copper film deposited on all three substrates, was determined using stripping voltammetry. The stripping voltammograms and the corresponding film thickness dependence on deposition time are shown in Fig. 3. The inset in Fig. 3, clearly shows a linear dependence of film thickness with time as expected.

In order to assess the surface morphology of the deposited copper film, deposition for 20 min under the same conditions as shown in Fig. 3 was performed on highly polished, substrates. The SEM images of the deposit on these highly polished samples are shown in Fig. 4a and b. The surface morphology showed a uniformly distributed film, made of well ordered, spherical grains with the diameter of ca. 100–150 nm. The EDX analysis (5 keV) shows that the deposited

film consists of 90% copper. It is likely that the spherical copper grains were probably formed in the flame and subsequently deposited on the surface rather than grown on the surface.

The Raman spectra of all samples analysed in Flame 1 are featureless, as could be expected for surfaces predominantly covered by elemental copper, Fig. 4c. These results are indirectly supported by the X-ray analysis used in here primarily for identifying the phases formed on the substrate surface and also for assessing whether and to which extent the copper was incorporated into the substrate structure. The X-ray pattern of the deposited substrate is shown in Fig.4 and corresponds to one obtained for 10Cu–90Fe alloy [18], and CuO [19] which is also shown in Fig. 4d. This result indicates that copper was incorporated in the unit cell of Fe (the major component of the carbon steel substrate). The observed diffusion and subsequent incorporation of copper (s.g. FM 3M, [20]), into the structure of iron (s.g. IM 3M,) is a result of an increase in mobility of copper atoms caused by the high temperature of the flame [15,18,21].

In a second set of experiments copper deposition was investigated in Flame 2 and Flame 3. In both flames the substrate was kept at the fixed height of 1.2 cm and deposition time was 20 min. As in Flame 1 experiments, blank experiments with aqueous solution containing no copper nitrate were carried out in oxidising flames as well, to ascertain the background effect on the sample. In this case the flames were oxidising due to high oxygen content, and as a result, the surface of the carbon steel samples were slightly oxidised, not shown. When copper was deposited using Flame 2 (or Flame 3), the deposit was dull grey and powdery with low adhesion. EDX analysis showed that deposited films typically contained 35 at.% of copper, 15 at.% of iron and 50 at.% of oxygen. Raman spectroscopy and XRD analysis of the surface sample deposited from Flame 2 are shown in Fig. 5a and b, respectively. The Raman spectrum of this sample shows narrow, strong peaks, which could not be ascribed to iron oxide/hydroxide species [22], (Fig. 5a). Instead, all the strong peaks observed at 166, 257, 412, 453, 504 and 711 cm^{-1}, can be ascribed to the $Cu_2(NO_3)(OH)_3$ known as mineral gerhardtite [23]. The formation of copper hydroxyl nitrate was confirmed by XRD analysis. The XRD pattern, (Fig. 5d) shows the presence of two phases with characteristic Fe peaks at 2θ 45, 65
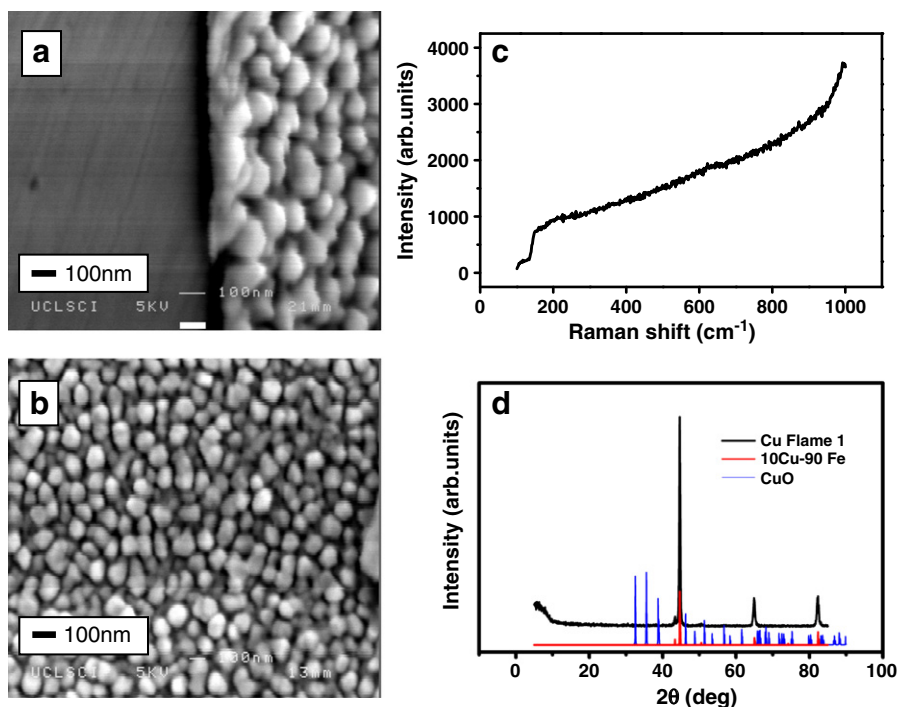
Fig. 4. a) and b) SEM images of copper deposited on polished samples, c the corresponding Raman spectrum and d the X-ray pattern (showing the XRD for CuO standard for comparison). Deposition was for 20 min in Flame 1 at fixed at 1.2 cm above the top of the burner, with 0.5 M copper nitrate added to the flame.
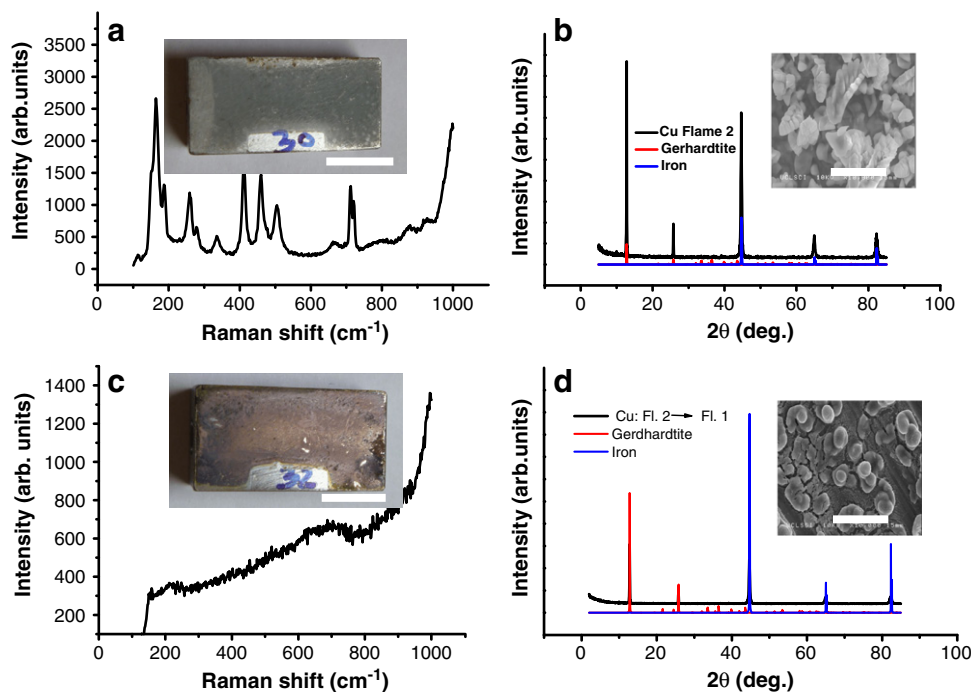

[17] E. Hadzifejzovic, J. Stankovic, S. Firth, P.F. McMillan, D.J. Caruana, Phys. Chem. Chem. Phys. 9 (2007) 5335.
[18] J. Eckert, J.C. Holzer, C.E. Krill, W.L. Johnson, J. Appl. Phys. 73 (1993) 2794.
[19] N.J. Calos, J.S. Forrester, G.B. Schaffer, J. Solid State Chem. 122 (1996) 273.
[20] StraumanM.E. , L.S. Yu, Acta Crystallogr. A 25 (1969) 676.
[21] X. Sauvage, F. Wetscher, P. Pareige, Acta Mater. 53 (2005) 2127.
[22] Q.M. Jin, J. Li, Y.L. Xu, X.S. Xiao, W. Zhang, L.Z. Jiang, Corros. Sci. 52 (2010) 2846.

[23] R.L. Frost, P. Leverett, P.A. Williams, M.L. Weier, K.L. Erickson, J. Raman Spectr. 35 (2004) 991.
[24] M.E. Strauman, S.M. Riad, Trans. Metall. Soc. Aime 233 (1965) 964.
[25] J.M. Aguirre, A. Gutierrez, O. Giraldo, J. Braz. Chem. Soc. 22 (2011) 546.
[26] H. Effenberger, Z. Kristall. 165 (1983) 127.