

TECHNICAL NOTE

CRIMINALISTICS

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Effect that the Relative Abundance of Copper Oxide and Zinc Oxide Corrosion has on the Visualization of Fingerprints Formed from Fingerprint Sweat Corrosion of Brass

ABSTRACT: From an examination of the fingerprint sweat corrosion of 40 different individuals on α phase brass, we show that an increase in visualization can be achieved by applying a negative potential to the brass followed by the introduction of a conducting powder. Previously, this technique has been demonstrated only for a positive applied potential and a corrosion product that was dominated by p-type copper (I) oxide. X-ray photoelectron and Auger electron spectroscopic analyses of the surface of the corroded brass show that an increase in visualization with a negative applied potential corresponds with an increase in the concentration of n-type zinc oxide relative to p-type copper (I) oxide with the Cu:Zn ratio <0.8:1. Work function conditions for the formation of an n-type zinc oxide/brass rectifying Schottky barrier are fulfilled.

KEYWORDS: forensic science, latent fingerprint, print visualization, metal corrosion, electrochemical mechanism, Schottky barrier

When latent fingerprints are deposited on metal surfaces, recent research has focused on fingerprint imaging techniques that exploit the chemical reaction that can occur between the metal surface and fingerprint deposit. This reaction, effectively a corrosion of the metal, results in a change in both the chemical and physical characteristics of the metal surface (1–4). We have shown how leaving fingerprint sweat deposits on planar brass disks in air at room temperature for several days produced sufficient corrosion of the brass to enable the fingerprint to be imaged even after the residue of the fingerprint deposit had been removed (3).

This visualization has so far been achieved by applying a positive potential (V) to the brass (~ 2.5 kV) followed by the introduction of a conducting carbon powder (grain size ~ 10 μm ; [3]). The introduction of the conducting powder is facilitated by using Cascade Developer (Foster and Freeman, Evesham, U.K.), which comprises ~ 400 - μm spherical beads that are coated with the conducting powder. By rolling the spherical beads back and forth across the charged brass surface, the conducting powder adheres preferentially to areas of corrosion on the metal thus enabling the fingerprint to be visualized. This technique has been used to visualize fingerprints on spent brass shell casings (5,6).

Adherence of the powder to areas of corrosion has been shown to be because of a potential difference (ΔV) between corroded and uncorroded brass with corroded areas having a potential lower than that applied to the un-corroded bulk, typically with ΔV up to 12 V for $V = 1400$ V (7). Further, we have discovered that this potential

difference is because of the junction between the corroded and uncorroded brass forming a rectifying metal-semiconductor contact known as a Schottky barrier (8). We have shown that a Schottky barrier is formed when the corrosion product comprises both copper (I) oxide and zinc oxide but is dominated by p-type copper (I) oxide with Cu:Zn = >3:1 (9). This type of rectifying metal-semiconductor contact requires the work function of the metal (ϕ_{brass}) to be less than the semiconductor ($\phi_{\text{s-c}}$), a condition satisfied for copper (I) oxide and α phase brass (7). The work function of a solid (ϕ) is defined as the minimum energy required to remove an electron from the Fermi level energy of the solid (E_{F}) to the vacuum level energy (10). When zinc oxide or copper (II) corrosion products dominate, a Schottky barrier is not observed (9).

In this technical note, we examine the effect that the polarity of V has on adherence of the conducting powder to the corrosion and visualization of the fingerprint. We then analyze the composition of the corrosion product with X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) and relate this to fingerprint visualization.

Experimental Details

Materials and Method

Forty donors each deposited fingerprint sweat onto 1-mm-thick, 25-mm-diameter α phase brass disks (68Cu-32Zn by percentage weight; [3,7,9]). All disks were left in air at room temperature ($18 \pm 5^\circ\text{C}$) for a period of 5 days, this time period being in keeping with our previous work (3). After the 5-day period, samples were washed in a 0.5 L solution of warm water containing a few drops of a commercial detergent, the disks being rubbed vigorously with a nonabrasive cloth to remove all traces of fingerprint deposit.

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TABLE 1—Grading system for determining the quality of ridge detail for enhanced fingerprints devised by Bandey (12).

Grade	Comments
0	No development
1	No continuous ridges. All discontinuous or dotted
2	One-third of mark continuous ridges. (Rest no development, dotted)
3	Two-thirds of mark continuous ridges. (Rest no development, dotted)
4	Full development. Whole mark continuous ridges

This washing regime has been shown to remove effectively the fingerprint deposit (but not the corrosion) from the surface of brass disks (11).

Each sample disk was then graded according to the quality of fingerprint ridge detail visible. For this, the grading system devised by Bandey (12) was used, and this is reproduced in Table 1. All samples were then subject to the fingerprint enhancement procedure described earlier with a positive $V = 2.5$ kV. The quality of fingerprint ridge detail was then reassessed. All samples were then washed as described previously to remove all traces of the conducting powder. The fingerprint enhancement procedure was then repeated on all samples but, this time, with a negative $V = -2.5$ kV. Each disk was then, once gain, graded according to the quality of fingerprint ridge detail visible.

Results and Discussion

After the initial grading, the majority of the 40 samples gave either a grade 1 or 2, which is in keeping with previous work (3). Following the application of the positive potential and conducting powder, 12 samples showed an increase in the Bandey grading, four by two grades and eight by one grade. Again, this is in keeping with previous results, and an increase in grading was observed only for samples that were graded 1 or 2 originally. After further washing, only four samples showed an increase in grading when the polarity of V was reversed (-2.5 kV), and these were different samples to those that showed an increase in grading with a positive V . All four of these samples showed an increase by only one grade and all four were graded as 1 initially.

A typical example of a sample that showed an increase in grading when a positive V and conducting powder were applied is shown in Fig. 1b compared with the original grading shown in Fig. 1a. For comparison, the sample after washing and application of a negative V and powder is shown in Fig. 1c.

A similar typical example, but with an increase in grading following the application of a negative V and conducting powder is shown in Fig. 2. Again, the sample after the application of a positive V and conducting powder is shown for comparison in Fig. 2b.

In both figures, it can be seen that a certain amount of powder has adhered to the sample when the polarity of V was opposite to that which produced an increase in grading. This is thought to be because of mechanical contact between Cascade Developer and the uneven surface of the corrosion, rather than an electrostatic effect. It has been shown previously that fingerprint sweat corrosion of brass can produce both raised and depressed features on the surface up to ~ 1 μm in depth (13), and we have shown how the contact angle between Cascade Developer and an object affects the tendency of Cascade Developer to “drop” powder (6).

All samples that showed an increase in grading when either a positive or a negative V and conducting powder were applied were then examined using XPS and AES. This was performed using a VG ESCALab 200d spectrometer (VG Scienta, Hastings, U.K.), Al

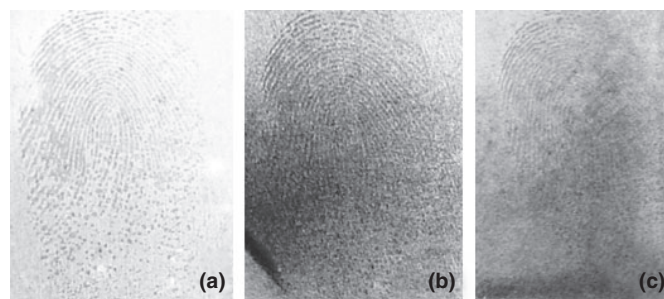


FIG. 1—Sample that showed an increase in grading following the application of a positive potential and conducting powder (b) compared with after washing (a) and after the application of a negative potential and conducting powder (c).

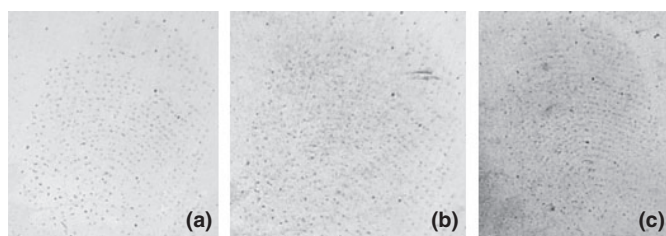


FIG. 2—Sample that showed an increase in grading following the application of a negative potential and conducting powder (c) compared with after washing (a) and after the application of a positive potential and conducting powder (b).

K α radiation (1486.6 eV) and a hemispherical analyzer. Individual high-resolution spectra were taken at a pass energy of 50 eV and an energy step of 0.05 eV.

XPS provides a quantitative measure of the elemental composition, oxidation state, and empirical formula of elements present in the surface layer (<10 nm) of a thin film. In addition, Auger transitions within the XPS spectra can give further information about the surface layer composition (14). While XPS is used routinely in the analysis of surface oxidation of both brass and copper (15,16), it has only been used recently to study the surface effects of fingerprint corrosion (9,17). Each of the 16 samples subject to XPS were analyzed on an area where the fingerprint sweat had corroded the brass.

The corrosion product of all 12 samples that showed an increase in grading with a positive V was dominated by copper (I) oxide although, in five samples, copper (II) hydroxide was also present. When copper (II) hydroxide was present, the Cu(I):Cu(II) ratio was $>6:1$. Zinc oxide was present in all samples although the Cu:Zn ratio was $>3.2:1$. These results support our previous observations as the relative abundance of corrosion products favors the formation of a p-type copper (I) oxide/brass rectifying Schottky barrier (9).

The four samples that showed an increase in grading with a negative V were dominated by zinc oxide with the Cu:Zn ratio being $<0.8:1$. In all samples, the copper was present as copper (II) hydroxide.

Four samples that failed to show any increase in grading with either a positive or a negative V were also examined by XPS and AES. These showed a mixed corrosion product of copper (I) oxide, copper (II) hydroxide and zinc oxide with no compound dominating. The Cu(I):Cu(II) ratio was typically $\sim 1.5:1$ and the Cu:Zn ratio typically $\sim 1.7:1$.

Figure 3 shows the copper (I) oxide AES spectra for typical samples that gave an increase in grading with a negative V (sample

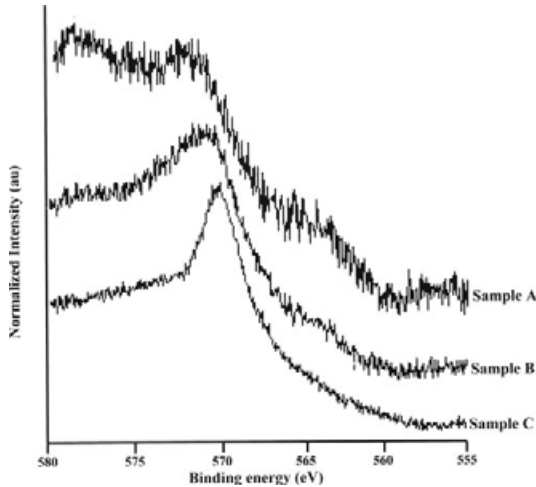


FIG. 3—Copper (I) oxide Auger electron spectroscopy spectra for typical samples that gave an increase in grading with a negative applied potential (A), a positive potential (C), or no increase in grading (B).

A), a positive V (sample C), or gave no increase in grading (sample B).

The clear peak in sample C corresponds to an Auger [Cu ($L_3M_{4,5}M_{4,5}$)] transition of 570 eV, which indicates the presence of copper (I) oxide. L_3 represents the core level electron ejected by the incident X-rays, and $M_{4,5}$ represents the initial level of both the relaxing electron and the emitted (auger) electron (18). This peak is absent in samples A and B.

Similar AES spectra are shown in Fig. 4 for zinc oxide. The decreasing intensity of the [Zn ($L_3M_{4,5}M_{4,5}$)] zinc oxide auger transition peak at 497.8 eV (15) between samples A and C shows the decreasing abundance (relative to copper) of zinc oxide as a corrosion product.

The clear inference from both the XPS and AES spectra is that when zinc oxide dominates the corrosion product, an increase in fingerprint visualization grading can be achieved, but with a negative (rather than a positive) V. Like copper (I) oxide, zinc oxide is also a semiconductor but is n-type rather than p-type (7). Thus, it would be expected that a negative V would lead to ΔV of sufficient magnitude to enable adherence of the conducting powder if the work function conditions for the formation of an n-type zinc

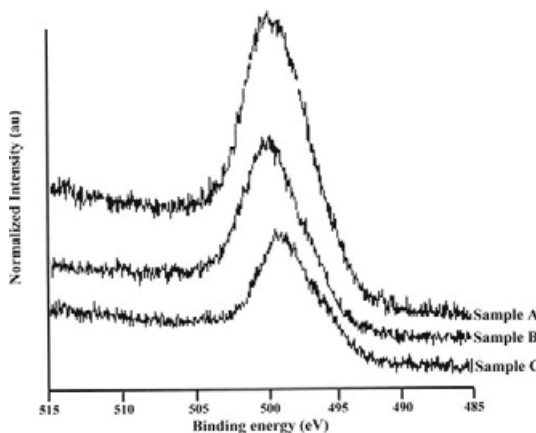


FIG. 4—Zinc oxide Auger electron spectroscopy spectra for typical samples that gave an increase in grading with a negative applied potential (A), a positive potential (C), or no increase in grading (B).

oxide/brass rectifying Schottky barrier were met. This type of rectifying metal-semiconductor contact requires the work function of the metal (ϕ_{brass}) to be greater than the semiconductor ($\phi_{\text{s-c}}$; [8]), a condition satisfied for zinc oxide and α phase brass (7).

Conclusion

Through a comparison of fingerprint sweat corrosion of α phase brass by 40 different individuals, we have demonstrated that applying either positive or negative potentials to the brass before introducing the conducting powder enhances visualization. The durability of the corrosion product on the surface of the brass enables these potentials to be applied in any order as, if an improvement in visualization is not obtained with one polarity, any conducting powder can be simply washed off and the process repeated with the opposite polarity.

Samples that gave an improvement in visualization with a negative V also showed dezincification of the brass with zinc oxide dominating the corrosion product. Surface concentrations of zinc greater than those expected for un-corroded brass (Cu:Zn = <2.2:1) are indicative of dezincification of the brass (19). While it is well known that increased chloride ion content accelerates dezincification (19), there is insufficient evidence from this study to suggest that increased dezincification results solely or mainly from an increased chloride ion concentration in the eccrine sweat of certain individuals. However, the number of samples that gave an improvement in visualization with a negative V was only one-third of those that gave an improvement with a positive V so, clearly, it is likely that variations in the composition of the sweat deposit (20) are affecting the galvanic corrosion process and the final relative abundance of corrosion product.

Use of a negative V may be of particular interest in regions of the world with a high ambient temperature as we have shown previously that fingerprint sweat corrosion of α phase brass in Iraq produces an increased surface concentration of zinc oxide relative to copper (I) oxide (17).

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