

## **Reliable irogane alloys and niiro patination—further study of production and application to jewelry**

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## RELIABLE IROGANE ALLOYS AND NIIRO PATINATION—FURTHER STUDY OF PRODUCTION AND APPLICATION TO JEWELRY

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### ABSTRACT

Japanese metalworkers use a wide range of irogane alloys (shakudo, shibuichi), which are colored with a single patination solution (niiro eki). This approach allows different alloys to be combined in one piece and patinated, producing a multi-colored piece of metalwork. At present the niiro patination process is unreliable. In this study we develop a deeper understanding of the effect of patination solution ingredients on color. We have tested a synthetic niiro solution, comparing the color results with traditional niiro solution patination. Surface products have been analyzed to determine how they are influenced by both the niiro solution and cleaning procedures during patination. A large range of shibuichi and shakudo alloys have been produced to determine the full color palette. This work also explores the use of alternative processes for the patination of irogane alloys, examining the effect of laser marking and anodizing on irogane alloys.

### INTRODUCTION

Developing a reliable niiro patination method has involved the combination of an artist skilled in the practices of Japanese alloy production and niiro patination with a materials scientist familiar with methods of analyzing and characterizing materials. In doing so it has been necessary to “reverse” engineer the traditional niiro solutions, which includes the traditionally produced material rokusho (a type of verdigris). Additionally, other traditional practices have been studied such as alloy casting techniques, the pre-patination treatment of surfaces using grated daikon radish, and polishing using traditional abrasives (deer horn and charcoal).

In our previous paper on the subject, the role of the ingredients in niiro solutions and the first attempts at producing a synthetic niiro solution from laboratory-

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grade chemicals were demonstrated. The products that formed on the surface were analyzed and identified, and a correlation was observed between these compounds and the quality of the colors achieved. An understanding of alloy production techniques and of the polishing and preparation procedures was developed, and methods of achieving the required surface finishes using both traditional and modern materials were explored. A method for the reliable and objective recording of the colors achieved was developed and a database was started, which records the colors achieved using different niiro solutions and a range of alloys. The subjective judgment of the artist was also included in this database (i.e., whether a color was 'good' or 'bad' from the artist's perspective).

The exact nature of the color produced by niiro patination is dependent upon a number of factors. The most obvious example of this variation is seen in the case of shakudo alloys, where the patination achieved with only 2 wt.% gold in the alloy is a deep blue/black color compared with the reds formed on pure copper. This dramatic change has been attributed to the presence of gold nano-particles within the copper oxide surface structure.<sup>1</sup> However, the causes of the other colors that can be produced using niiro patination have not yet been fully studied

On shibuichi alloys (silver and copper), where copper is only part of the structure, the colors obtained are quite different. The microstructure of Ag/Cu alloys consists of the copper-rich phase surrounded by the Ag/Cu eutectic phase. The overall effect is to modify the bright silver color to a moderate gray. The differing silver-to-copper ratios in shibuichi alloys thus produce differing gray shades, but exactly what is occurring at the surface is not yet fully understood.

In this paper the methods that can generate a wide palette of colors when using copper, silver and a range of shakudo and shibuichi alloys are described. The colors have been recorded objectively but also judged subjectively by the artist. This paper also describes the continuing development of a reliable synthetic niiro solution. Detailed analytical analysis of the effect of salt content in the solution on the patinated surface is discussed. It is also shown how the techniques employed by the craftsperson play an important role in the color that is produced. The effects of procedures recommended in traditional texts (e.g., surface cleaning during patination) have been examined in terms of the changes they impart to the surface.

In the search for new methods and processes that can improve or enhance the traditional niiro methods, alternative technologies for patinating the alloy surfaces have also been explored, specifically the application of electrochemical methods to niiro solutions and the use of laser marking technology to modify the surface of the alloys. By doing this work it is hoped that the techniques can become more widely adopted as some of the 'luck' and 'black art' associated with niiro patination have been removed. At the same time it reveals how such long-established methods still hold many mysteries and how the knowledge and craft of the practicing artist is still important to the production of beautiful objects.



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## EXPERIMENTAL PROCEDURES

### Analytical Techniques

#### *Scanning Electron Microscopy (SEM)*

Scanning electron microscopy (SEM) was used to observe the microstructures of the alloys and the appearance of the niiro surfaces. Quantitative elemental analysis of the regions of interest was carried out using energy dispersive x-ray analysis (EDX). SEM was carried out using an FEI XL30 ESEM instrument equipped with an Oxford Instruments INCA energy dispersive x-ray analyzer. Imaging was conducted in both topographic mode (secondary electrons) and atomic number contrast mode (back scattered electrons or BSE). EDX was used to quantitatively measure the elements present at the surface of the patinated alloys. Note that very thin layers ( $<2\mu\text{m}$ ) analyzed in this way will produce results that over-represent the elements in the substrate due to the electron beam interaction volume.

#### *X-ray Diffraction*

X-ray diffraction (XRD) was used to identify the phases present in the alloys. XRD gives crystallographic information on the phases present and can also provide information on the effect of rolling in terms of the alignment of certain crystal planes with the rolling direction. XRD was carried out on a PAN Analytical MPD diffractometer using Cu K $\alpha$  radiation. XRD was used in the glancing angle configuration in order to identify the phases present at the surface of the experimental niiro materials. In this configuration the incident x-rays were directed at the sample with an incident angle of  $0.5^\circ$ , which makes the resulting diffraction pattern more sensitive to phases present only on the surface (e.g., surface oxides, etc.).

#### *Color Measurements*

A Minolta Colorimeter was used to objectively measure the color of the patinated samples. The results from the Minolta CMD508D Colorimeter are recorded in the L\*a\*b\* system, more correctly known as the CIE 1976 (L\*a\*b\*) color space. Positive numbers for a\* represent the red colors and negative numbers tend towards the green. Similarly for the b\* axis, positive numbers tend towards yellow and negative values towards the blue. L\* varies between 0 and 100, where no light is reflected (black) and 100 is total reflection (diffuse white).

### The Color Range of Shakudo and Shibuichi Alloys Patinated in Niiro Solution

A range of shakudo alloys (Cu/Au) with gold percentage 0.5%, 1%, 2%, 3%, 4%, 5%, 7.5%, 10%, 13%, 16%, 20%, and a range of shibuichi alloys (Cu/Ag) with silver percentage 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% were produced in the workshop using a small induction furnace (for the lower melting temperature

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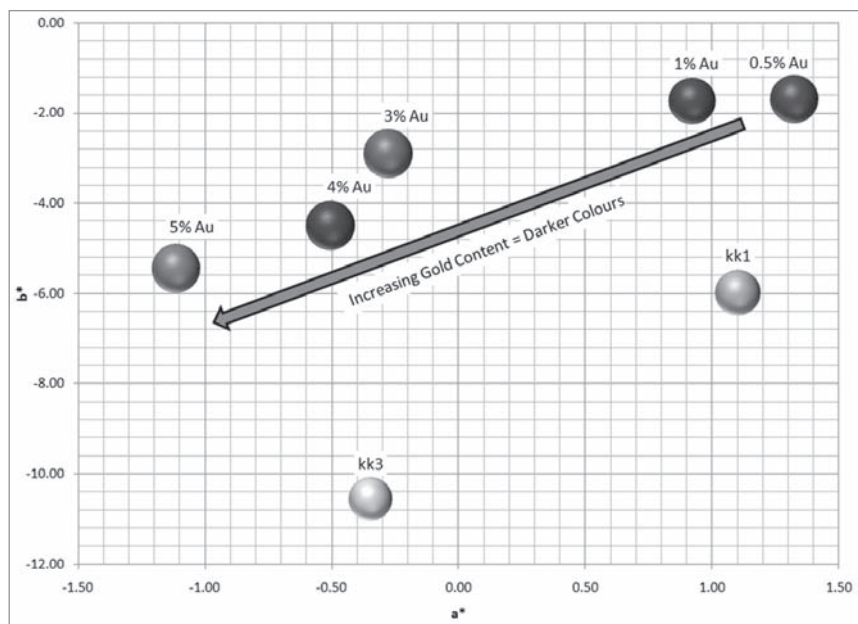
alloys) and a resistance furnace (for the higher melting temperature alloys). The alloys were cast into steel molds, milled, cleaned and rolled, using best practice as discussed in our first paper.<sup>2</sup>

### *Shakudo Alloy Color Range*

The shakudo alloy samples were polished using charcoal and pumice, finishing with 1200 silicon carbide powder. They were patinated using a solution of 3g rokusho, 3g copper sulfate, 1L H<sub>2</sub>O at 60°C (140°F) for 60 minutes. (This solution/time/temperature was selected as representing an average niiro patination.) The lower gold-content shakudo alloys patinated to a range of colors from dark brown (0.5%Au), becoming progressively darker to a dark blue/black (5%Au). Shakudo alloys purchased in Japan from Komokin were patinated to compare results (see Table 1). Colorimeter readings for all the shakudo patination tests are given in Figure 1.

*Table 1* Komokin shakudo alloys

Element	Komokin 3:100Au	Komokin 1:100Au
Cu weight%	93.9	96.8
As weight%	1.4	1.5
Ag weight%	1.9	0.8
Au weight%	2.9	0.9



**Figure 1** Effect of gold content on colors produced on shakudo alloys.  
Alloys KK1 and KK3 are arsenic-containing alloys traditionally produced in Japan and produce much darker colors.

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The higher gold-content shakudo alloys were not patinated successfully. The 7.5% Au shakudo did produce a dark blue/black patina layer, but it was not as dense or even as the patina formed on the lower gold-content alloys. The higher gold-content alloys were progressively less successful in patination, with the 20% Au shakudo forming very little surface color. The alloys were repolished and repatinated many times without success. A number of different patination solutions was also tried, including the solution recommended by Oguchi for the patination of shakudo (2.1g rokusho, 1.2g copper sulfate, 0.2g alum, 1L H<sub>2</sub>O).<sup>3</sup> Extended patination times up to 48 hours were tried, again without success. These results correspond with reports from Japanese craftspeople that high gold-content shakudo alloys are very difficult to patinate. However, Oguchi reported successful patination of shakudo alloys after repeated recleaning and repatination (described by him as “a series of troublesome operations”) with a gold-content up to 30%, which produced a purple color. Further study of this area is needed to identify the conditions necessary to reliably patinate high gold-content shakudo.

### *Shibuichi Alloy Color Range*

In the past the range of shibuichi alloys traditionally used for niiro patination has typically only covered a narrow range of compositions (25-60wt% Ag) and therefore the full potential for the colors possible using this alloy system has not been explored. The shibuichi alloys were solder inlayed into a fine silver sheet and polished with silicon carbide paper and finished with pumice powder. The inlayed sheet was patinated in a solution of 3g rokusho, 3g copper sulfate, 1L H<sub>2</sub>O at 40°C (104°F) for 30 minutes. The sheet was dipped in grated radish prior to patination.<sup>2</sup> (This solution/time/temperature represents an average niiro patination for shibuichi alloys.) The patinated alloys produced an even range from dark gray (10Ag90Cu) to light gray (90Ag10Cu). See Figure 2 for colorimeter measurement of the patination colors.<sup>4</sup>

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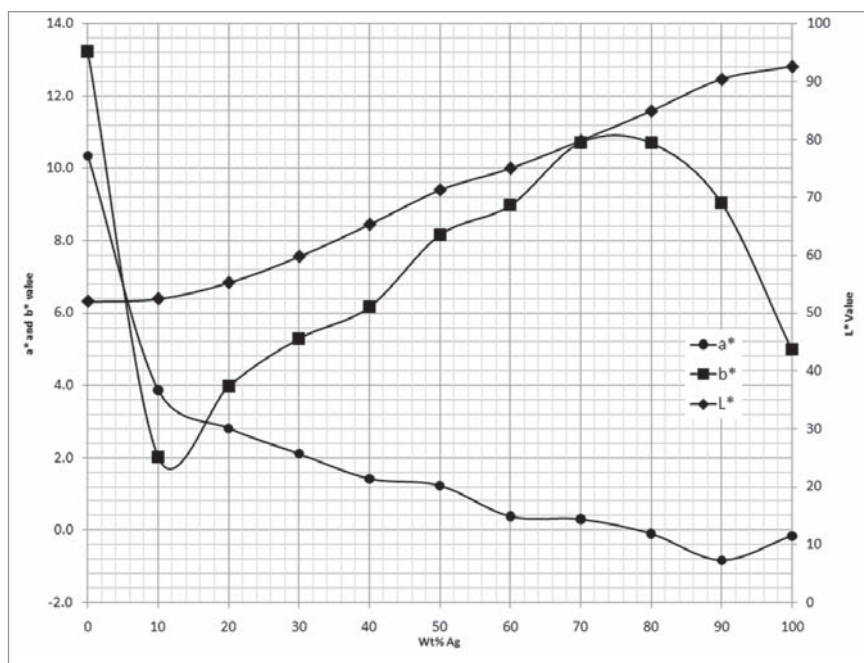
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**Figure 2** The variation in the patination color ( $a^*$ ,  $b^*$  and  $L^*$ ) for the range of shibuichi alloys (0 to 100% Ag)

In Figure 2 the variation of  $L^*$ ,  $a^*$  and  $b^*$  is shown where  $L^*$  is the lightness, negative values of  $a^*$  indicate green while positive values indicate magenta/red, and negative values of  $b^*$  indicate blue and positive values indicate yellow. The weight % of silver in copper is shown on the x-axis, and both  $a^*$  and  $b^*$  are shown on the left y-axis while  $L^*$  is shown on the right y-axis.

As Figure 2 shows, the lightness ( $L^*$ ) of the patination colors increases in a consistent and almost linear fashion from 100%Cu to 100%Ag. However, the  $a^*$  value drops suddenly from 100%Cu, and with only 10%Ag it has reduced from  $a^*=10$  to  $a^*=4$ . After this initial drop the reduction in  $a^*$ , or redness, falls consistently with increasing silver content with the lowest value being  $a^*=-0.8$ , indicating a slight move into the green region.

For  $b^*$  the variation is more complex. Initially there is a large fall from  $b^*=13$  to  $b^*=2$  with the addition of 10%Ag, indicating a large drop in the yellow component of color. However, after this initial drop the  $b^*$  value increases again from  $b^*=2$  at 10%Ag to  $b^*=10.8$  at 70%Ag, an increase in the yellow component of the color. There is then a reversal of that trend above ~75%Ag and the  $b^*$  value falls rapidly from  $b^*=10.8$  to  $b^*=4.9$  at 100%Ag. This reversal of the trend for  $b^*$  (yellowness) is probably related to the microstructure of the alloy above ~70%Ag, which is close to the eutectic for Ag-Cu, with higher amounts of the alpha phase occurring as the amount of Ag increases above this point. Of course, the actual perceived colors depend upon the combination of  $a^*$  and  $b^*$  (and to some extent  $L^*$ ) with, for example, at 50%Ag  $a^*=1.5$  and  $b^*=8.1$ , resulting in a color that would be described as 'medium gray' by the craftsperson.

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## Comparison of Synthetic Niiro Solution with Traditional Niiro Solution

In our 2009 Santa Fe Symposium paper we described the development of a synthetic niiro solution (5g copper sulfate, 2.65g copper acetate, and 0.65g sodium chloride, 1L H<sub>2</sub>O) based on XRF and XRD analysis of rokusho. In order to further evaluate this solution, we conducted tests on multiple alloys and compared results with those for traditional niiro solutions.

Multiple alloy sample sheets were produced by soldering together strips of pure copper (oxygen-free CW008/C103), fine silver, 2%Au shakudo, 50Ag50Cu shibuichi, and 25Ag75Cu shibuichi. The sheets were polished using silicon carbide papers and then finished with powdered pumice or 1200 silicon carbide powder (high polish). The sheets were patinated in either a synthetic niiro solution or a traditional niiro solution (5g rokusho, 5g copper sulfate, 1L H<sub>2</sub>O). The sheets were dipped in grated daikon radish prior to patination. Colorimeter measurement results for the patinated colors are given in Table 2. The results show that our synthetic solution has achieved colors similar to the traditional solutions.

*Table 2 Comparison of synthetic niiro solution with traditional niiro solution*

		Synthetic Niiro	Synthetic Niiro (high polish)	Traditional Niiro	Traditional Niiro (high polish)
2% Shakudo	L*	41.7	41.6	47.2	42.6
	a*	0.0	0.3	-0.80	-0.1
	b*	-5.3	-6.7	-6.1	-3.6
100% Cu	L*	48.4	48.7	52.4	44.8
	a*	18.5	18.6	12.8	17.1
	b*	17.4	2.3	14.7	14.6
Fine silver	L*	90.1	95.3	92.7	83.3
	a*	0.1	0.0	-0.2	0.6
	b*	5.3	6.8	5.8	8.6
50Ag50Cu	L*	80.8	84.2	78.9	92.7
	a*	0.4	0.2	0.6	0.7
	b*	6.0	6.3	9.1	7.5
25Ag75Cu	L*	61.1	69.3	60.9	63.3
	a*	1.8	1.8	0.6	1.3
	b*	4.6	4.2	6.1	8.1





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## Salt Content of the Niiro Solution

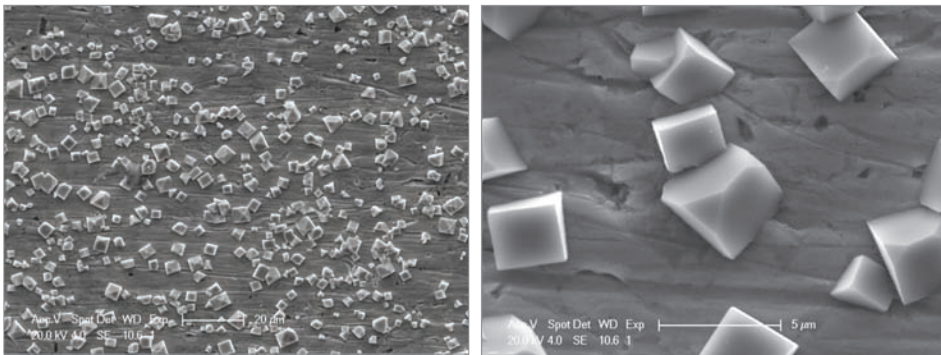
In our previous work we had observed that the presence of the correct level of salt (NaCl) appeared to be crucial for the best colors (i.e., too low or too high and the colors were far from optimum). The results from SEM/EDX show that Cl appears to be an integral part of the compounds that formed on the surface. In order to determinewhether the salt was a necessary ingredient of the niiro solution and to help discern its role in the patination process, a patination run was carried out in a niiro solution containing no chlorides.

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A pure copper alloy was patinated in a synthetic niiro solution containing only copper acetate and copper sulfate (no NaCl). The piece was patinated in the normal manner but the color produced was judged to be 'streaky' and weak. XRD of the surface products revealed that the only phase present was  $\text{Cu}_2\text{O}$ .

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*Figure 3 SEM image of the surface of copper after patination in a solution containing no salt*

Jones

EDX of the large crystals confirms the presence of Cu and O in the expected ratio for  $\text{Cu}_2\text{O}$ . From this result it appears that the absence of Cl seems to inhibit the formation of the oxide and, where oxide does grow, it is concentrated in a small number of relatively large crystals. The surface surrounding the large crystals did show an increased O content but it is clear that any oxide layer in these regions is very thin.

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## When Salt Is Too High

It is clear from the results above that the presence of chlorides in the niiro solution is necessary for good patination results. However, too much salt appears to also have a detrimental result on the quality of the patination color. A solution described in the literature by Ard contains 6g copper acetate, 1.5g copper sulfate, 1.5g salt.<sup>5</sup> The salt content in this niiro solution is higher than in the solution being tested in this study. Fine silver and shakudo (2%Au) were used as test pieces in this solution because they are the materials most obviously affected by the formation of chlorides.

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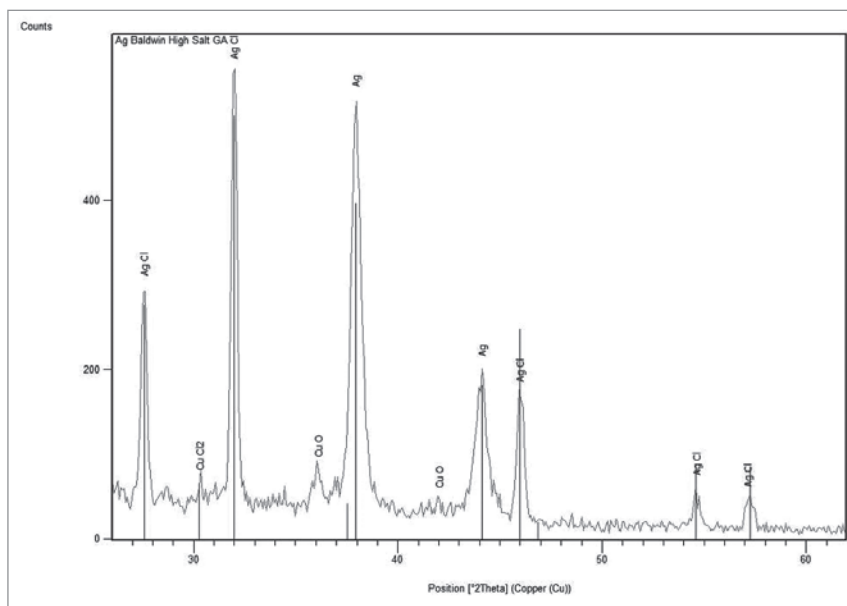
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Examination of the fine silver reveals that the resulting color was brown and uneven in nature. SEM/EDX showed the brown patches to consist of a crystalline material high in Cl. XRD confirmed that the surface products were silver chlorides (AgCl) with virtually no oxides detected.



*Figure 4 XRD trace from the surface of fine silver after patination in a high salt-containing nitro*

On the copper the color was orange to brown and with very uneven coverage. The surface product was revealed by XRD to be primarily  $\text{Cu}_2\text{O}$  but with significant levels of  $\text{CuCl}$ .

### The Purple Problem

On several occasions the shibuichi alloys produced a patchy purple color after patination. XRD and SEM/EDX analysis confirmed that only  $\text{Cu}_2\text{O}$  was present on the surface albeit with ~2 wt.% Cl associated with the larger  $\text{Cu}_2\text{O}$  crystals. It is apparent from the literature that it is common for silver chlorides to photodecompose and in doing so produce a purple compound.<sup>6</sup> It appears that a small amount of silver chloride was formed (presumably below the detection limit of XRD) and this has decomposed after exposure to light or heat, forming the purple color. However, these samples were treated in the same way as all others so it is not clear why this only happens on occasion.

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## The Influence of Cleaning during Patination Treatment

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It is well known among practitioners of niiro patination that to avoid streaky and uneven colors it is important to clean and degrease a work piece prior to patination. Many craftspeople also recommend that the workpiece should be removed from the patination bath after a short period, cleaned again using sodium bicarbonate and then returned to the niiro solution. Some craftspeople will repeat this procedure more than one time. However, there is no published explanation as to why this improves the end result or what it achieves.

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In order to study this phenomenon a number of multi-alloy samples was patinated in the synthetic niiro solution. One sample was simply patinated for 60 minutes and rinsed in clean water at the end of the process. The other was lightly cleaned using a cloth and sodium bicarbonate powder at 10 minutes and at the end of the 60 minutes. It was observed that the untouched samples generally had a duller and less pleasing appearance than the cleaned samples.

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The samples were examined using SEM and EDX in order to determine the products that were formed on the untouched sample and what the cleaning process did to these products. In the SEM images below (Figure 5 to Figure 9), the surfaces of the two multi-strips, cleaned and untouched, are compared side by side.

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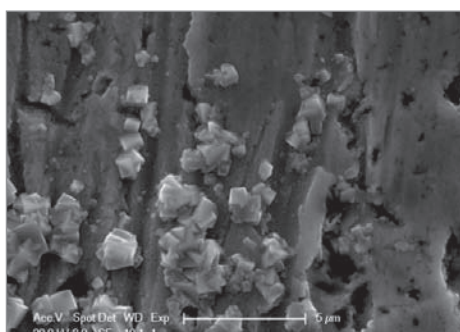
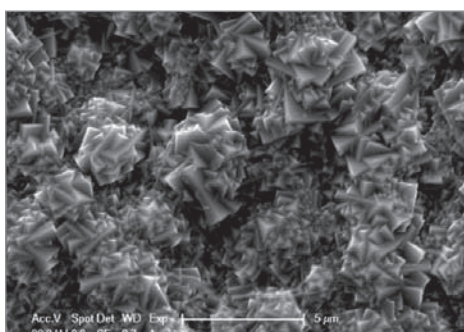
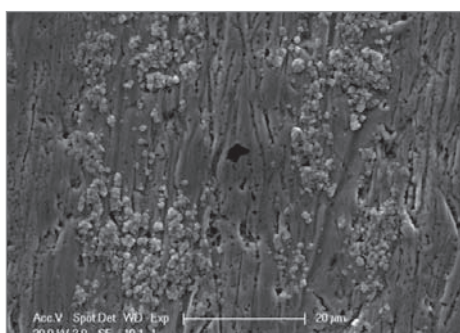
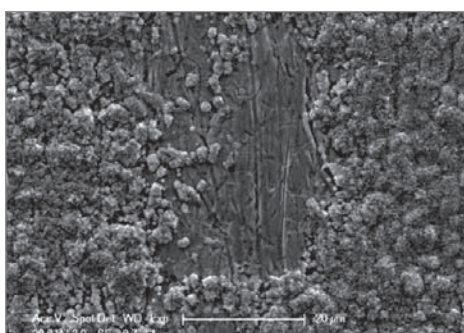
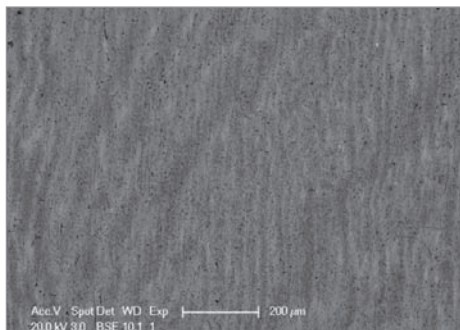
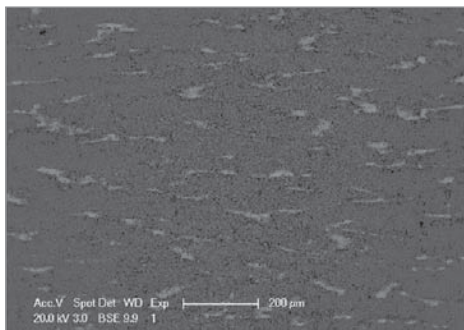
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Untouched

Cleaned (10 minutes & 60 minutes)



**Figure 5** SEM images from the untouched (left column) and cleaned (right column) surface of a shakudo (2%Au) sample. Magnification increases from top to bottom.

The untouched shakudo surface is covered in a relatively thick layer of large crystals but in regions, the underlying alloy can be observed at holes in this layer (see top left image in Figure 5). Note this is using atomic number contrast. EDX analysis of the crystals is shown below in Table 3. After cleaning, the underlying microstructure is clearly visible using atomic number contrast (top right image in Figure 5), indicating that any surface is now substantially thinner than was the case before cleaning.





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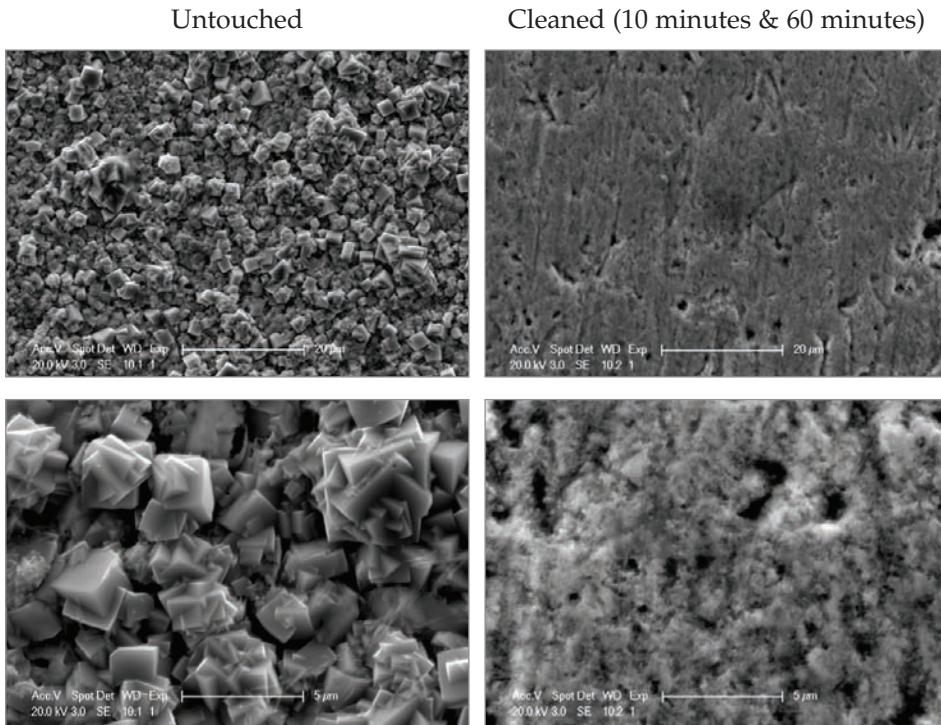
Shakudo (2%Au)	Large Crystals (untouched)	Underlying Surface (untouched)	Cleaned Surface
Element	Atomic%	Atomic%	Atomic%
O	36.2	13.0	31.0
Cl	4.7	0.3	3.1
Cu	58.9	85.6	65.0
Au	0.2	1.2	1.0

**Table 3** EDX of the large crystals and the underlying surface  
observed on the untouched shakudo (2%Au) sample

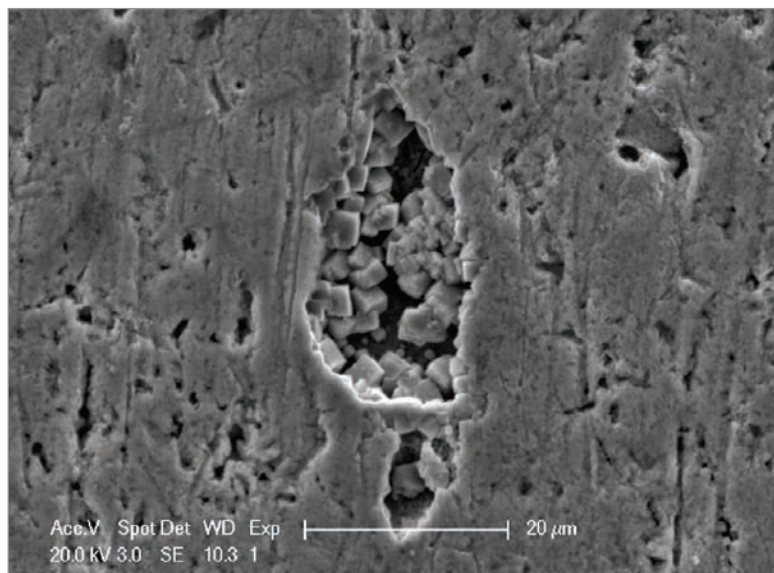
The EDX results from both the untouched and cleaned surface of shakudo are consistent with the compound present being  $\text{Cu}_2\text{O}$ . However, the larger crystals appear to contain a significant level (~5 at.%) of Cl. The underlying surface beneath the layer of large crystals appears to be much lower in both O and Cl and shows a relatively high level of gold (equivalent of ~4 wt.%). In comparison, the cleaned surface shows an elemental composition more similar to that of the large crystals than the underlying surface.

This result suggests two things: first, that the large oxide crystals grow preferentially on the low gold regions of the microstructure and second, that the action of cleaning with a cloth and sodium bicarbonate has not simply removed the large oxygen-rich crystals but has in some way thinned and smeared this layer evenly over the whole surface, covering up any holes in the layer but also removing any large crystals.





**Figure 6** SEM images from the untouched (left column) and cleaned (right column) surface of a pure copper sample. Magnification increases from top to bottom.



**Figure 7** SEM image of the surface of a cleaned copper alloy showing the surface layer to be smeared over the top of the large crystals (sub-surface crystals)





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The EDX from the copper alloy reveals that the large crystals are very similar to those observed on shakudo (i.e.,  $\text{Cu}_2\text{O}$  with ~5 wt.% Cl). The cleaned surface is also similar in terms of O and Cu but has an elevated Cl level. The crystals observed below the clean surface (Figure 7) have an identical composition to those observed on the untouched surface. It is thus possible to conclude that, like the shakudo alloy, the process of cleaning the sample after patination actually serves to smear a layer over the existing oxide crystals, possibly removing or breaking down the larger crystals.

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**Table 4** EDX analysis results from different regions on the untouched and cleaned pure copper sample surface

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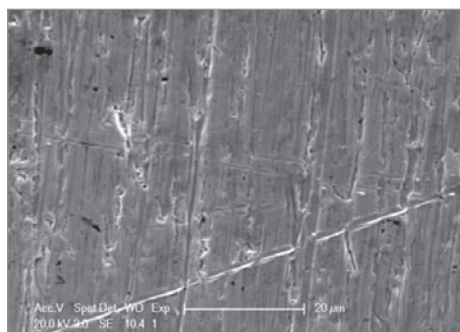
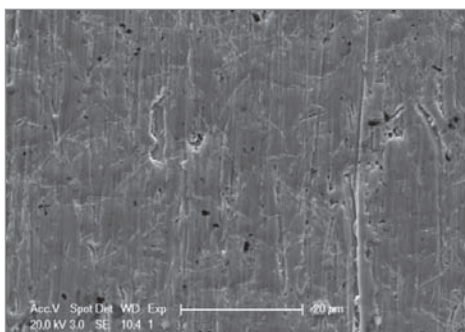
Pure Cu	Large Crystals (untouched)	Cleaned Surface	Sub-surface Crystals (cleaned surface)
Element	Atomic%	Atomic%	Atomic%
O	33.3	29.7	35.0
Cl	5.1	11.6	4.3
Cu	61.5	58.7	60.7

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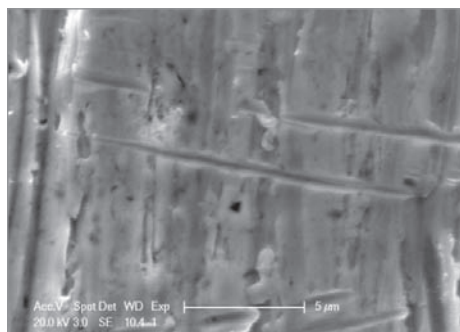
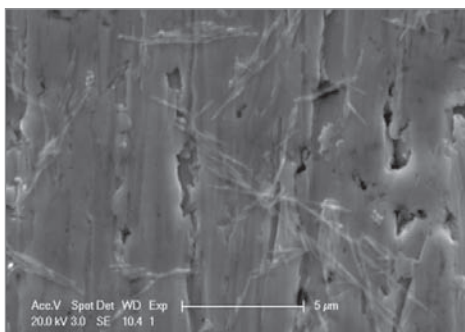
Untouched

Cleaned (10 minutes &amp; 60 minutes)



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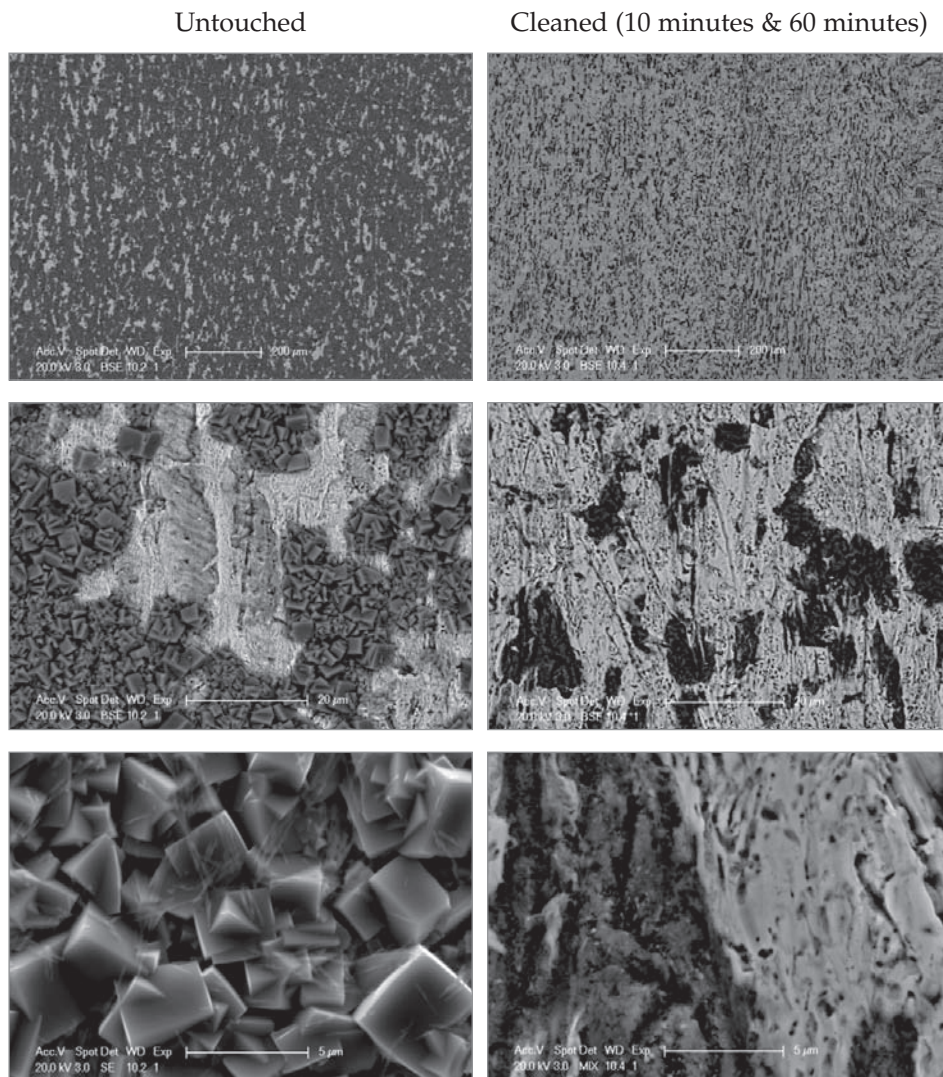
**Figure 8** SEM images from the untouched (left column) and cleaned (right column) surface of a fine silver sample. Magnification increases from top to bottom.







Fine silver is virtually unaffected by both the patination and the cleaning process, with the appearance and elemental composition being unchanged with no oxide or chloride formation.



**Figure 9** SEM images from the untouched (left column) and cleaned (right column) surface of a shibuichi (50/50) alloy. Magnification increases from top to bottom.

The shibuichi alloys in the untouched state exhibit a relatively thick and patchy layer of crystal growth (dark regions in top left and center left image in Figure 9). The crystals appear to prefer to grow on the copper-rich phase. After cleaning, this layer of crystals appears to be completely removed, revealing the underlying microstructure (top right and center, Figure 9). Closer inspection and

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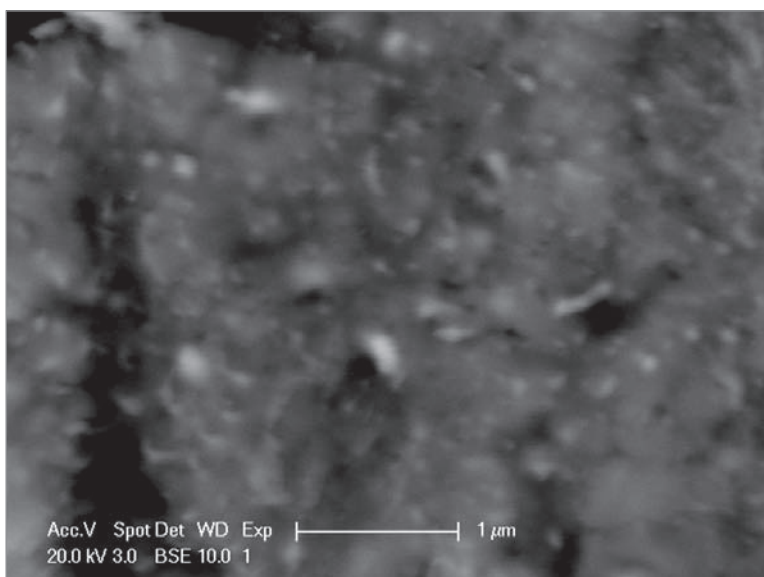
EDX analysis shows that the silver-rich regions (bright regions in bottom left image of Figure 9) remain almost entirely unaffected by the niiro or the cleaning (it does contain some Cu, thus the Cu and O content in this analysis). The copper-rich regions (dark regions in bottom left image of Figure 9) are covered in a very fine layer of oxide containing nano-particles of silver-rich materials as shown in Figure 10.

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**Figure 10** High magnification SEM image (atomic number contrast) of the surface of the copper-rich phase in the shibuichi alloy after patination and cleaning. Note the nano-sized bright particles of silver-rich material in the Cu-O-rich layer.

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**Table 5** EDX results from the Ag- and Cu-rich regions of the shibuichi alloy after patination and cleaning

Shibuichi (50/50)	Ag-rich Area (cleaned)	Cu-rich Area (cleaned)
Element	Atomic%	Atomic%
O	4.3	40.1
Cl	0.8	3.1
Cu	16.4	48.6
Ag	78.5	8.2

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## Conclusions from SEM/EDX Study of Patinated Alloy Surfaces

- A synthetic niiro solution consisting of 5g copper sulfate, 2.65g copper acetate, and 0.65g sodium chloride in 1L of de-ionized H<sub>2</sub>O has been formulated, and it is found that good and reproducible niiro patination colors on a wide range of alloys are possible using this formulation. The colors compare well with those produced using more traditional solutions.
- Salt (NaCl) in the niiro solution is necessary for good colors but if levels are too high, then the formation of chlorides occurs, which reduces the quality of the colors produced.
- The colors produced are a result of the formation of Cu<sub>2</sub>O on the surface, but good colors are only achieved when the surface layers also contain a significant amount of chlorine (between ~5 and 10 at.% has been observed).
- No Cl-containing phases were detected by XRD, although phases below the detection level of XRD (~1-2 wt.%) or amorphous phases are possibly present. The occasional presence of a purple color on the surface of shibuichi alloys indicates that some AgCl may be forming and breaking down under exposure to light or heat.
- On shakudo the color is formed when the Cu<sub>2</sub>O contains nano-sized gold particles (although they have not been observed in this work) but it appears that Cl is also necessary for a good color and finish.
- On shibuichi the silver is largely unaffected but the copper-rich phase is oxidized, and this Cu<sub>2</sub>O layer appears to contain nano-particles of silver. Chlorine in the oxide layer is again necessary for good colors on this material.
- Fine silver is almost completely unaffected by the niiro and the cleaning process, although it has been previously observed that the application of grated radish (daikon) is necessary to prevent the formation of AgCl on fine silver.
- The commonly recommended process of cleaning the surface of the workpiece during the patination process (with sodium bicarbonate) results in brighter patina colors. The cleaning process results in the removal of layers of large crystals (~5µm) but also thins and smears the oxide layer over the surface, covering over gaps in the surface layer and also covering over some of the larger crystals.

## Electrolytic Experiments

In order to explore ways of improving niiro patination methods, a series of experiments were conducted where the principles of anodizing were applied. In the case of aluminum, anodizing is used to promote the growth of an oxide film on the surface of the metal. Relatively high potentials have to be used as the oxide film naturally formed on the surface of aluminum is passive and protects against the further formation of oxides. By making the metal the anode and applying a direct current through a conductive solution (the electrolyte) at a potential normally in the range 15 to 30V, the oxide film on aluminum can be made thicker.

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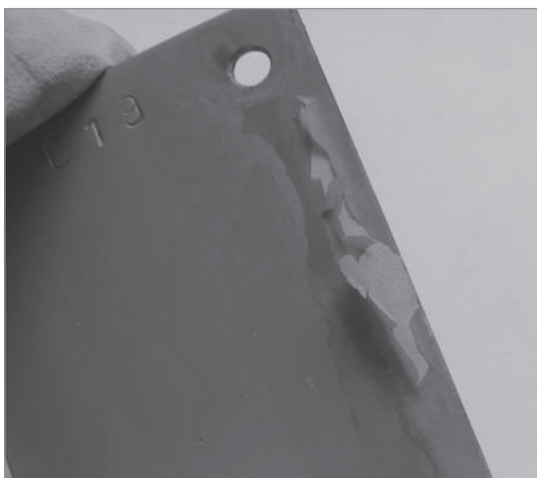
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It was therefore considered appropriate to apply the anodizing technique to the irogane alloys. The alloys are not naturally passivating and as such a lower potential should be required to promote oxide growth. The sample to be patinated was used as an anode in an electrochemical cell with a niiro solution as the electrolytic solution and a pure copper sheet as the cathode (generally it is best to avoid contamination of the niiro solution with iron-based materials). Voltages of 5, 10 and 20V were used at times ranging from 5 to 60 minutes. Typical currents were in the range 200 to 300mA. The samples were regularly checked to monitor the change of color and the general appearance of the sample (e.g., for signs of streaks and uneven coverage, etc.).

Two types of samples were used; initially pure copper samples measuring ~50mm x 70mm were used to test the experimental set up. Multi-strips ~50mm x 100mm consisting of each of the alloys soldered together were used in order to simultaneously test the range of alloys under identical conditions. Samples were judged on their color in a subjective manner and compared with samples produced in the solution without applied current. Selected samples were also subject to XRD to determine the phases present on the surface.

## Results

At 5V and 10 minutes pure copper appeared to have discolored significantly, but the color was brighter and more orange than that normally achieved using niiro alone. Increasing time and/or voltage (up to 20V) did not appear to improve or significantly change the color. It was noted that at times above 5 minutes the layer that was forming on the surface of the pure copper was prone to flaking off, especially around the edges of the samples. This effect got worse with time in the solution.



**Figure 11** *The flaky nature of the layer formed on pure copper after anodizing at 20V for 10 minutes*

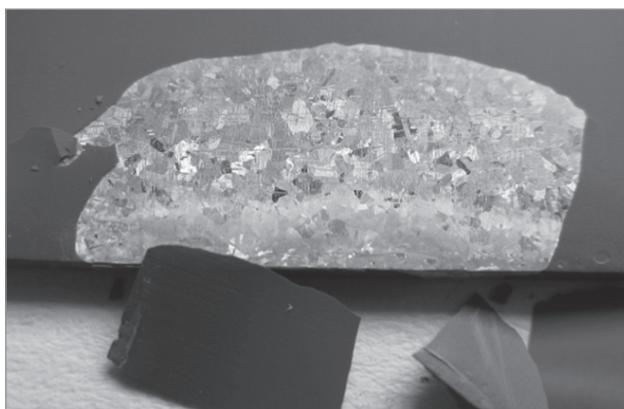


On the multi-strip samples, which were tested at 5V and for various times (5 minute to 20 minutes), the colors produced are shown in Table 6.

**Table 6** Colors produced by the use of anodizing in a synthetic niiro solution

Material	Shakudo	Pure Cu	Fine Ag	Shibuichi 50/50	Shibuichi 25/75
5min/5V	Patchy black	Dull orange	Brown, in regions	Green	Dark green
10min/5V	Black	Orange	Brown, full cover	Green	Dark green
20min/5V	Black	Bright orange, flaking	Brown, flaking	Green	Dark green

On the pure copper and the pure silver, the surface color became increasingly flaky with time in the solution and eventually the surface layer would fall off, revealing the clean and etched metal surface beneath as shown in Figure 12. The surface layers on all other alloys appeared adherent and could not be easily removed.



**Figure 12** The flakey nature of the surface product and the underlying electrolytically etched silver surface (fine silver)

### XRD of Pure Copper Anodized in Niiro Solution

XRD analysis was used to identify the phases forming on the surface of the pure copper samples subject to the anodizing treatment. A typical example is shown in Figure 13 (from a pure copper sample run at 20V and 10 minutes). It is clear that the procedure has produced a thick layer of  $\text{Cu}_2\text{O}$  but also that there is a very significant presence of copper chloride,  $\text{CuCl}$ . It is known from our previous work that the formation of  $\text{CuCl}$  is usually an indicator of a poor-quality color. By







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comparison the niiro solution alone, with no current, produces good colors and the phase formed on the surface is primarily  $\text{Cu}_2\text{O}$ .

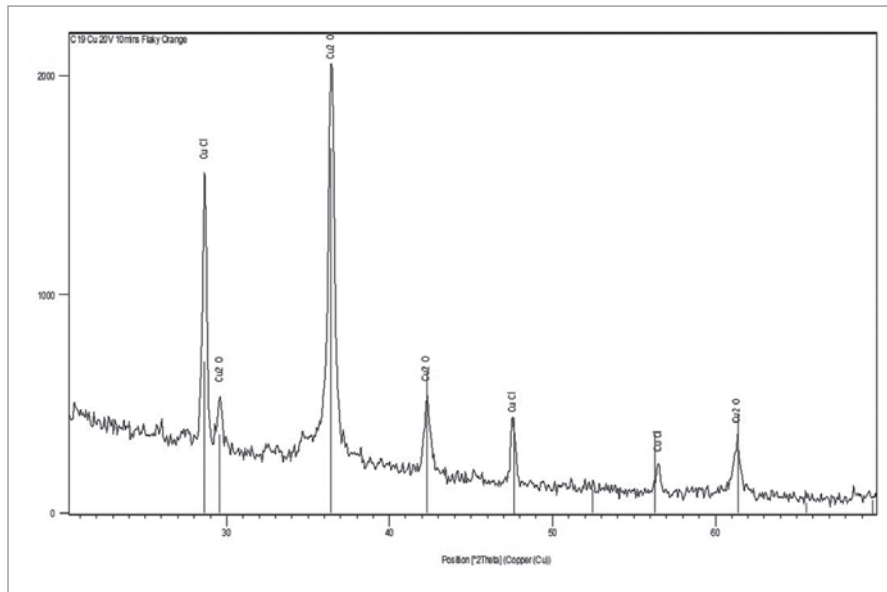
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Similarly for the multi-strip samples, the colors produced (brown on fine silver and greens on the shibuichi alloys) are indicative of the formation of chloride phases. These alloys, when patinated in the same niiro without current, produced acceptable colors.

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**Figure 13** XRD (grazing incidence) trace from the surface of a pure copper sample that was anodized for 10 minutes at 20V, producing a flaky bright orange surface. Note the clear presence of  $\text{CuCl}$  in addition to  $\text{Cu}_2\text{O}$ .

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## Conclusions

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It appears, therefore, that the use of anodizing does not speed up or improve the color or consistency of niiro patination but instead favors the production of chloride phases on the surface, which produces poor colors and leads to poorly adherent layers on copper and fine silver. It may be possible to improve on these results by using niiro solutions of different compositions (e.g., reduced or zero salt) but this is beyond the scope of this current study.

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## LASER PATINATION

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Work by O'Hana et al. has shown that laser marking technology can be used to produce a wide range of attractive colors on titanium jewelry.<sup>7</sup> The laser marking technology produces thin oxide layers on the titanium (90Ti6Al4V) surface whose thickness is such that it produces interference colors on the titanium, such layer



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being between 35 and 200nm according to O'Hana, who matched her observed colors to the work on thickness by Perez del Pino<sup>8</sup> and Goldsmiths.<sup>9</sup> The colors vary with the layer thickness, which can be achieved by varying how much heat the laser imparts to a particular area. Because the laser is generally used at a fixed power, the amount of heat imparted to the surface is simply related to the dwell time over a particular area, which is itself controlled by the speed at which the laser spot traverses the surface.

Since it has been shown that niir patination is primarily a result of the growth of oxygen-rich surface layers on the alloys being patinated,<sup>2</sup> then it would seem that a laser marking technology may also be applied to produce patinated surfaces on the shakudo and shibuichi alloys. There is also some mention in the literature of flame torches being used to produce patination on these alloys, and laser marking could be regarded as a form of micro-flame patination.<sup>10</sup> The advantages it may bring include rapid processing (1cm<sup>2</sup> can be marked in a few seconds) and reproducible colors as the only variables are the laser parameters (which can be tightly controlled) and the alloy itself. Other advantages could include the patination of selected areas of a piece or the reproduction of complex patterns by using computer-generated designs that can be fed to the laser path control system.

In order to explore the effect of laser marking on the patination colors, we were granted access to the laser facilities at The Laser Processing Research Centre at The University of Manchester, Manchester, UK (Head of Centre, Professor Lin Li). Dr. Sarah O'Hana and Dr. David Whitehead (The University of Manchester) assisted with the set up and processing of the materials on their equipment. In particular, Dr. O'Hana designed the patterns that were applied to the alloys and determined the initial conditions (e.g., traverse speed, hatch size, etc.) using the software, which controls the laser marking machine.

The equipment used was a Laserline - Laserval Violino 532 Laser Marker with a diode pumped Nd:YVO<sub>4</sub> laser source, 7W max power and with a 3-axis sample stage. The metal pieces tested were in two forms, small samples ~25mm x 50mm x 1mm and large samples 50mm x 100mm x 1mm. The patterns used to mark the sample were either in the form of a square concentric pattern or a square pattern produced in a left to right, top to bottom raster fashion. On the small samples the square concentric patterns were ~5mm x 5mm. On the larger samples the squares were ~17mm x 17mm. The alloys tested were pure copper (99.9%), shakudo (2%Au) and two types of shibuichi (Ag with 25%Cu and 50%Cu). They were in the as-rolled condition and had been polished using pumice.

In order to explore the possible variations in color, the laser flux experienced by the surface was varied by varying the speed at which the laser spot traversed the surface. The laser speed was varied from 50mm/s to 500mm/s. The laser spot size was 50μm but the distance between adjacent laser tracks (the hatch) was set to 50 or 100μm. The phases that were formed on the surface were analyzed using both SEM/EDX and grazing incidence XRD. Cross sections were also prepared to examine the thickness and microstructure that had been produced.

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## Results

### *Optical Images and IFM*

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**Figure 14** Shikudo (2%Au) alloy laser marked using square raster patterns. The laser speed for each square was, left to right top row, 50 to 500mm/s steps of 50mm/s.

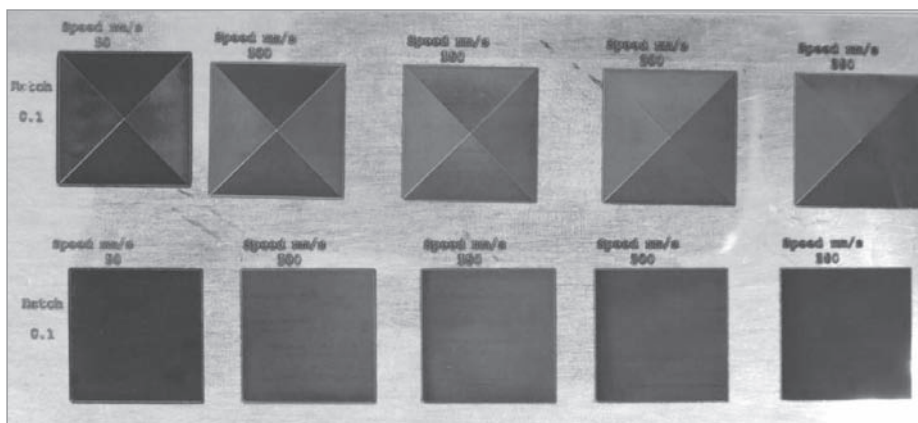
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For the pure copper and shikudo (2%Au) samples, the general trend in color was from a matte black at the slowest laser speeds (i.e., the highest heat input) to less dark colors being produced as the speed increased. Below 250mm/minute the colors were very pale and the change in color was more likely a result of a change in the morphology of the surface (i.e., the melting and re-freezing of the surface) than the formation of oxides. The results for pure copper and shikudo (2%Au) were virtually identical.

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**Figure 15** Shibuichi (50/50) alloy laser marked using both square concentric patterns (top) and square raster patterns (bottom). The laser speed for each square was (left to right) 50, 100, 150, 200, 250mm/s.

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For the shibuichi alloys (25Ag75Cu and 50Ag50Cu) the colors produced were very similar for both alloys. The lowest laser speeds (50mm/s) producing a matte black color; however, faster speeds produced a lighter color initially and then a progressive darkening. The color change compared to the unmarked alloy at high speeds was more pronounced than for the case of the copper and shakudo.

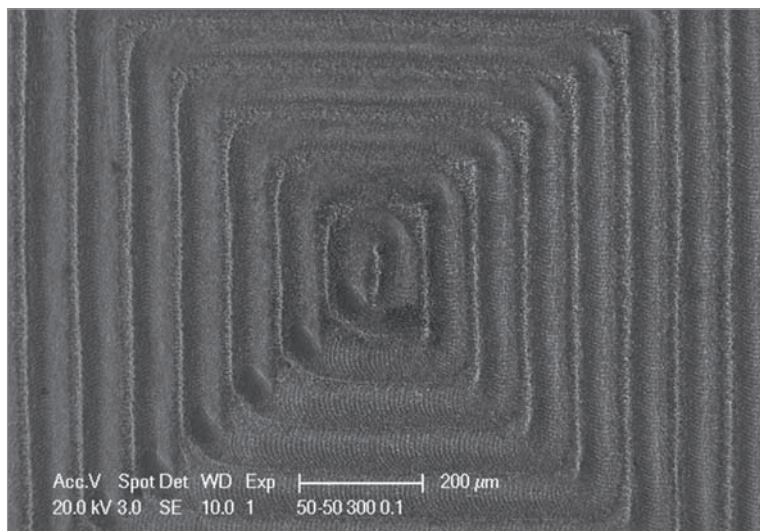
An interesting phenomenon was observed when a square concentric pattern was used to apply the laser marking. The resulting pattern consisted of four triangular quarters (i.e., as if viewing a square pyramid from above). Each quarter was observed to have quite different colors. For example, on the pure copper samples the colors within a single square pattern varied from a deep green to a light golden color.

## SEM Results from the Laser-Marked Alloys

### *Surfaces*

SEM observation of the surfaces formed by the laser marking process shows that the marked area consists of parallel tracks where the laser has passed, each consisting of a series of curved overlapping regions of re-solidified layers. These regions are caused by the pulses of the laser, each resulting in a discrete event where material is melted and/or vaporized. As the laser spot moves on, the next area is affected, causing it to overlap with the previous zone.

The appearance of the material suggests that the surface has been melted (and possibly vaporized) by the laser forming overlapping circular regions of rapidly cooled and re-solidified material. The higher the laser speed the less these circular regions overlapped, and for slower speeds these circular regions overlapped to a greater extent.



**Figure 16** SEM image of a laser mark made using the square concentric pattern on shibuichi (50/50) at 300mm/s





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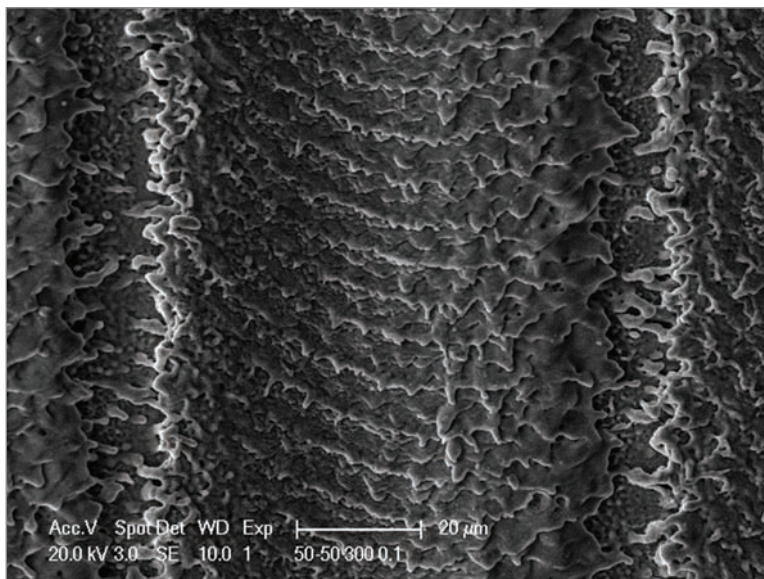
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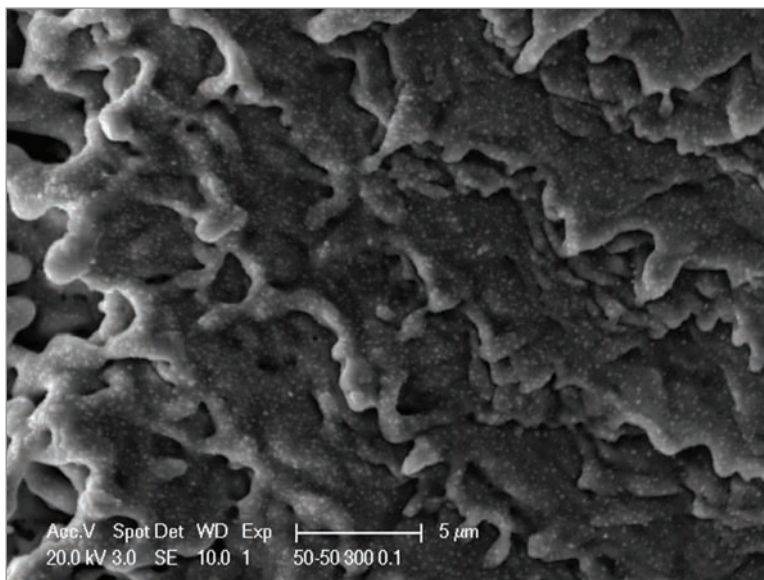
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*Figure 17 SEM image of a single track on the laser mark (square concentric) made on shibuichi (50/50) at 300mm/s*



*Figure 18 Close-up of the laser track on shibuichi (50/50) made at 300mm/s. Note the small, round features on the surface of the re-solidified material.*







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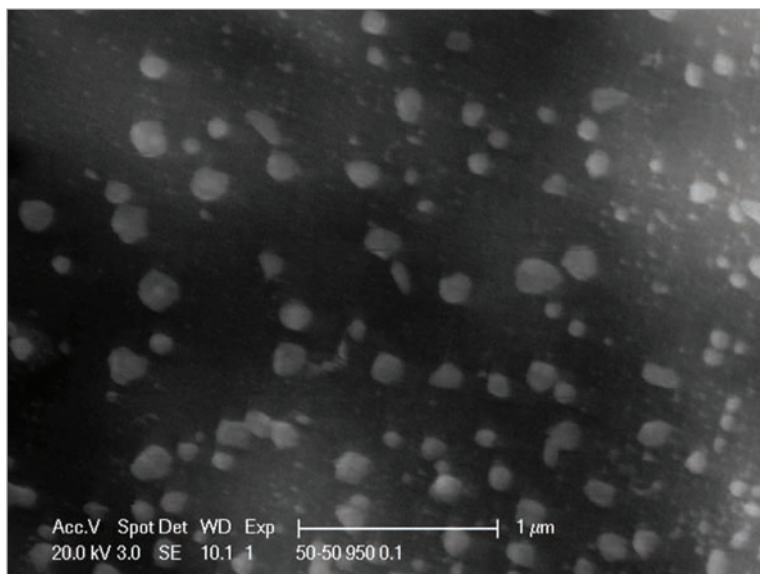
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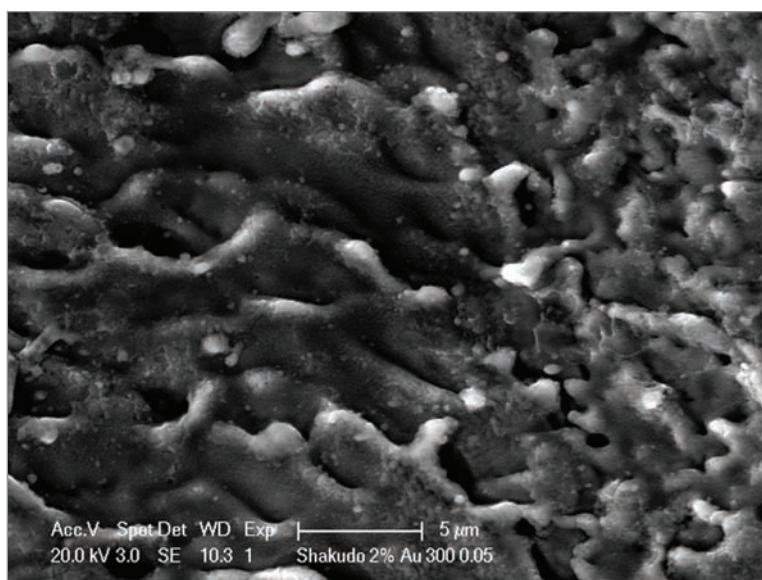
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**Figure 19** Close-up showing the fine particulate features observed on the surface of the re-solidified material of a laser marked shibuichi (50/50)

High magnification of the laser track revealed a complex structure. In the shibuichi (50Ag50Cu) the re-solidified layer appeared to have small (~200nm) precipitates evenly distributed on the surface of the re-solidified layer. These were too small to be meaningfully analyzed using EDX and so it was not possible to discern their composition.



**Figure 20** Close-up of the surface of laser-marked shakudo (2%Au) marked at 300mm/s.

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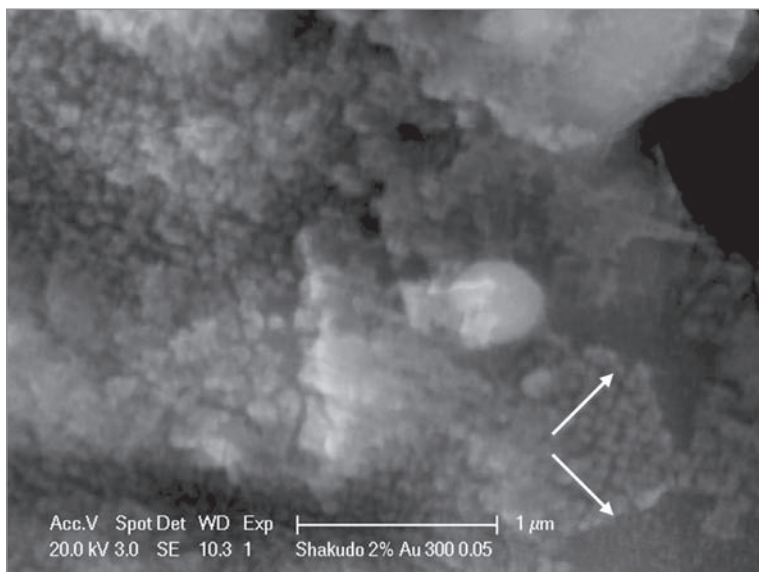
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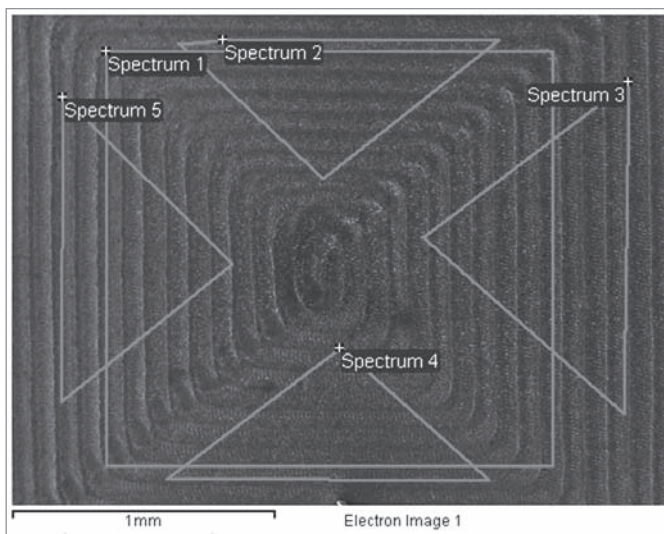
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*Figure 21 Close-up of the surface of the laser-marked shakudo showing the surface 'crust' and regions where it appears to be missing (marked), revealing its thickness to be <200nm*

In the shakudo and copper samples the surface of the re-solidified regions appeared to be uniformly covered in a very thin (<100nm) 'crust' of material that in places had flaked away, revealing the underlying material as shown in Figure 21. Compared to the surfaces on titanium observed by O'Hana et al.,<sup>6</sup> these surfaces are considerably rougher, and clearly more melting, vaporization and re-freezing of the surfaces have occurred. SEM and EDX carried out on the four quarters of a mark made using the square concentric pattern (i.e., where each quarter was observed to be a different color) showed no significant difference in the chemical composition in each quarter.



Weight % EDX results

Spectrum	O	Cu	Au	Total
Spectrum 1	10.1	85.8	4.1	100.0
Spectrum 2	11.3	84.8	3.9	100.0
Spectrum 3	11.1	84.7	4.2	100.0
Spectrum 4	10.7	85.4	3.9	100.0
Spectrum 5	11.4	84.9	3.7	100.0

**Figure 22** SEM image and EDX results from the surface of a laser-marked shakudo (2%Au). Note the similarity of the results for each of the quarters indicated, which appear as different colors to the naked eye. (Note: 10 wt.% O is ~ 30 wt.%, 85 wt.% Cu ~ 60 wt.%)

However, there were subtle differences in the appearance of the different segments as shown below in Figure 23. The surface shows the overlapping individual laser melting events but on opposite sides of the concentric square their appearance is distinctly different, with the right side showing a more rounded pattern while the left side shows a more linear, overlapping feature. It is not known why this is affecting the color produced, but differences in the amount of reflected light and the thickness of the oxide layers may play a part in this.





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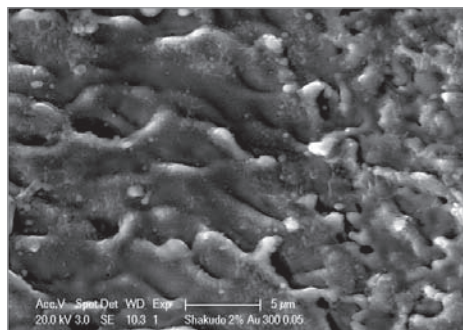
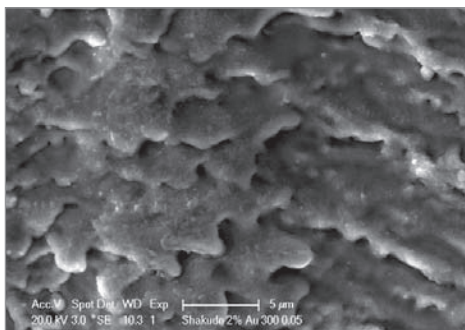
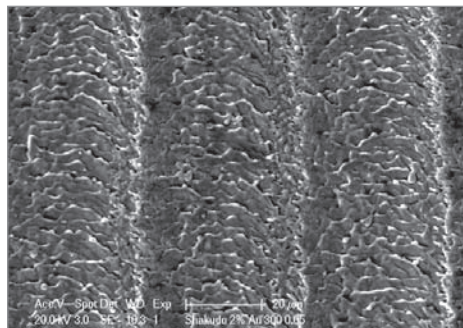
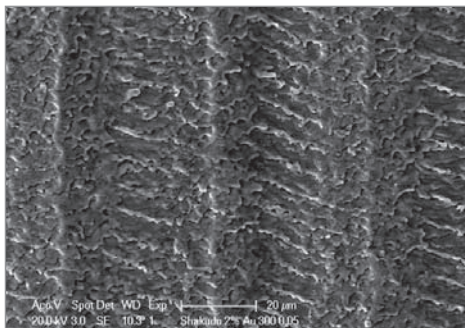
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**Figure 23** SEM images of the laser-marked surface of shakudo (2%Au) alloys (300mm/minute, hatch 0.05mm). Left column is from the left side of a concentric square pattern and the right column is from the opposing right quadrant.

### Cross-sectional SEM

A cross section of the laser-marked materials was prepared and examined using SEM/EDX. It was extremely difficult to observe the surface layers due to the fact that they were so thin and due to difficulty obtaining the correct contrast levels (using atomic number contrast) to show the structure of the coating. However, it was observed that on pure copper the re-solidified surface layers were  $<1\mu\text{m}$  in thickness in most places and consisted of a mixture of dark and bright phases. This suggests a mixture of an oxide layer and re-solidified metal particles (with the metal being the brighter phase).





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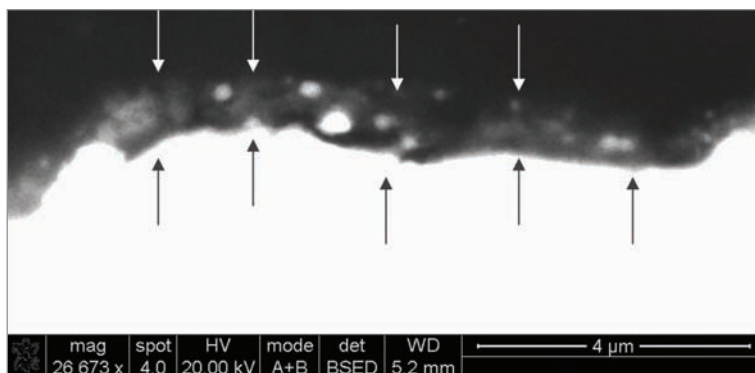
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**Figure 24** SEM image (atomic number contrast) of a cross section of laser-marked pure Cu showing thin surface layer consisting of both light and dark phases (light = higher atomic number, dark = low atomic number)

### XRD Results

On the pure copper sample the XRD grazing incidence ( $0.5^\circ$ ) data was taken from the darkest square, which had been made using a laser traverse speed of 50mm/s. The XRD trace shows that in addition to the Cu of the substrate there are peaks, which indicate the presence of both CuO (cupric oxide) and Cu<sub>2</sub>O (cuprous oxide or cuprite). Compared with our previous results for the niiro patination of pure copper,<sup>2</sup> this result is different in two ways. First, the signal from the copper oxide phases is much lower in the case of the laser-marked materials, indicating a thinner or less crystalline layer compared with the niiro patination. Second, in our previous work the niiro-patinated material showed no evidence of cuprite (CuO) on the surface. Since cuprite is a black material and cupric oxide is a red compound, the presence of cuprite in the surface layers of the laser marked sample is apparently responsible for the darker colors produced.

On the shibuichi alloys it was even more difficult to obtain an XRD signal from the surface, suggesting a very thin and/or amorphous layer. However, because of the colors produced (i.e., matte blacks and browns), it is probable that CuO was also forming on these surfaces.





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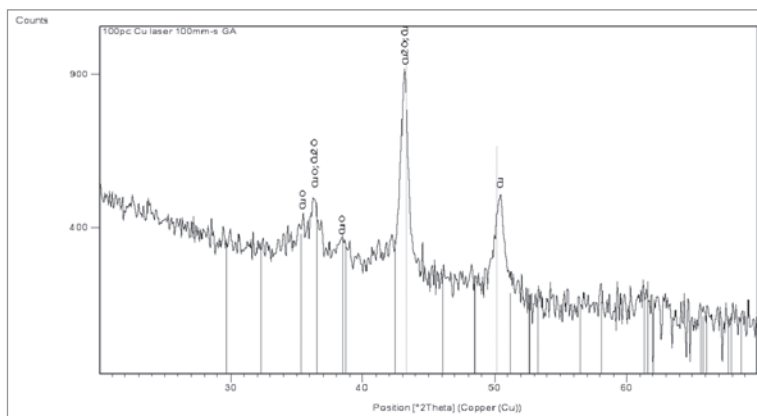
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**Figure 25** XRD (grazing incidence,  $0.5^\circ 2\theta$ ) from laser-marked pure Cu showing Cu (substrate), CuO (red line) and Cu<sub>2</sub>O (blue line)

## Conclusions from Laser Work

The use of laser marking technology on titanium alloys has been shown by O'Hana et al. to produce a thin oxide layer (20nm to 350nm), producing interference colors which are highly attractive and useful in the production of jewelry. However, the use of the same technology on alloys of copper, silver and gold (i.e., shakudo and shibuichi alloys) does not produce the same range of colors as titanium alloys. Laser marking produced surfaces that had undergone significant melting, vaporization and rapid solidification. This is perhaps not surprising given the different melting points (m.p.) of the material (90Ti6Al4V m.p.~1600°C/2912°F, Cu m.p.~1084°C/1983°F, Ag m.p.~960°C/1760°F). While the observed surface layers are still thin (~1µm), they are too thick to produce interference colors.

The main aim, though, was not to produce interference colors but to try and replicate the colors produced by the niiro patination process, which is known to produce colors through the formation of oxides of copper and with gold or silver nano-particles contributing to the color. The layers that were produced by laser marking appeared to consist of a mixture of oxidized material and re-solidified metallic material. SEM images suggest that the oxidation appears to have taken place at the surface of the melted/re-solidified material. X-ray diffraction of the surface layers has revealed that the copper is oxidized to both CuO (curpric oxide) and Cu<sub>2</sub>O (cuprous oxide). Since CuO is black and Cu<sub>2</sub>O is red, it is probable that the dark colors obtained by laser marking are a result of the formation of CuO in the surface layers. It is known from previous work on niiro patination that the dominant phase in the red-colored patina on copper is red Cu<sub>2</sub>O. The rapid cooling experienced by the materials as it re-solidifies after being melted and/or vaporized may result in a number of phenomenon including non-stoichiometric phases, the formation of thermodynamically unstable phases or even amorphous material. The rapid nature of the process may also limit the type of oxide that can form as the material is only hot enough to be oxidized for a very short time.



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The surfaces also have a high degree of surface roughness and topography compared with the as-polished surface due to the melting and re-solidification surface, and this roughness/topography gives rise to a matte finish to any surface color.

While laser marking does change the color and oxidize the surface of copper, shakudo and shibuichi, the type and nature of the oxidation is significantly different from that produced by the niiro patination process. The higher temperatures, rapid heating and cooling rates and the change in surface topography are the main reasons for these differences. The colors were not judged to be comparable with niiro patination.

Despite the incompatibility with the expected niiro colors, there was some appeal in the square concentric samples that exhibited different colors on each quadrant, ranging from golden browns to greens. There is clearly some morphological difference, which depends upon the direction in which the laser beam was traversing the sample surface. However, there is no significant difference in the chemical composition in the different quadrants. This suggests that the difference lies in the amount of light scattered and possibly the thickness of the oxide layer that is formed. It has been suggested that the laser beam is polarized and thus may have a different effect when traversing in different directions.

## SUMMARY

In this work the full palette of colors that are possible when using niiro patination on copper, silver, shakudo and shibuichi alloys has been produced and recorded. In particular, a wider compositional range for shibuichi alloys (10 to 90 wt% Ag) than ever previously reported has been produced and patinated. The details of the methods and the database of colors that has been produced will be a valuable tool for the jewelry designer who wants to begin to use these methods to make unusual and unique, multi-colored work. In particular, the recording of the colors in an objective manner (using the CIE 1976 L\*a\*b\*) allows CAD programs to accurately render the color that can be expected to be produced on a piece.

The literature on the subject of niiro patination includes a wide range of possible compositions for the niiro patination solution, many of which involve the use of traditional materials such as rokusho. Such ingredients are often hard to source outside of Japan, and their use makes control over the reliability and repeatability of the process difficult. This work has successfully tested a synthetic niiro solution, made from readily available standard laboratory-grade chemicals. It has been shown to produce colors comparable with the traditional solutions in a consistent manner. Its use can eliminate some of the uncertainty in the process and allow the craftsperson to better control the end result.

As with any craft-based methods, there is still some variability inherent in the process. Even though the consistency of the niiro solution was improved, questions remained over the exact nature of the surface and the role of traditional procedures such as cleaning, polishing, etc. By using modern analytical techniques it has been possible to analyze the exact nature of the surface products

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and determine how they are influenced by both the niiro solution and the cleaning procedures.

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The surfaces are dominated by the formation of thin layers of  $\text{Cu}_2\text{O}$  in all cases, but the presence of a significant amount of Cl appears to be necessary for the formation of strong and pleasing colors. In the silver-bearing alloys only the copper-rich phases contribute significantly to the oxide layers, and the presence of nano-sized silver particles in the oxide layers on shibuichi alloys appears to be responsible for the colors that are formed. In shakudo alloys there is evidence that the oxide prefers to grow on the areas with a low gold content, and in high gold-containing alloys the formation of oxide is inhibited to the point where good patination is difficult to achieve.

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The use of 'cleaning' part way through the patination process has always been part of the traditional process but the exact effect it has on the surface structure has never been studied. This work has shown that on copper and shakudo alloys, cleaning with a cloth and bicarbonate of soda results in the transformation of the large ( $\sim 5\mu\text{m}$ )  $\text{Cu}_2\text{O}$  crystals into a smoother surface and the filling in of any voids in the surface layer. However, the surface still consists of  $\text{Cu}_2\text{O}$  but with a much finer crystalline structure. On shibuichi the larger crystals observed on the non-cleaned surface are mostly removed by cleaning, revealing the underlying alloy microstructure but with the copper-rich regions being oxidized and containing silver nano-particles. Fine silver is largely unaffected by the patination process or the cleaning.

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This work has also explored the use of novel and alternative processes to the niiro patination of irogane alloys. However, it was found that both laser marking and anodizing did not produce better colors or improve reliability. Even though interesting results were achieved, including some new colors, further work would be needed to fully understand the behavior of the alloys in these processes if they were to be optimized for use by craftspeople.

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#### REFERENCES

1. Masahiro Kitada, "Microstructures and Physical Properties of Colored Layer of Cu-4mass%AU Alloy (Shakudo) Fabricated by Japanese Traditional Technique," *J. Japan Inst. Metals* 69, no. 12 (2005): 1069-1076.
2. C. O'Dubhghaill and A.H. Jones, "Japanese Irogane Alloys and Patination—A Study of Production and Application," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2009*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2009).

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3. Hachiro Oguchi, "Experimental Studies on Japanese Traditional Coloring Copper," *Bulletin of the Faculty of Fine Arts, Tokyo University of Arts* no. 8 (September 1972): 23-84.
4. C. Ó Dubhghaill and A.H. Jones, "Metal Mosaics, Customizing Designs with Homemade Alloys," *MJSA Journal* (February 2010): 28-34.
5. William Ard, "Return to the Forge: Extended Research into Mokume-Gane and Granulation," *Metalsmith Papers* (Tampa, Florida: Society of North American Goldsmiths, 1981).
6. F. Yalcinkaya and E.T. Powner, "Ag/AgCl/Cl<sup>-</sup> Coated Silver Stripe Reference Electrode," *Medical Eng Phys* 19, no. 3 (April 2007): 299-301.
7. Sarah O'Hana, Andrew J. Pinkerton et al., *Surface Engineering* 24, no. 2, (2008): 147. DOI 10.1179/174329408X315607.
8. A. Perez del Pino, J.M. Fernandez-Pradas, P. Serra and J.L. Morenza, *Surf. Coat. Technol* 187, no. 1 (2004): 106-112.
9. Goldsmiths, "Coloured Refractory Metals for Jewellery," *Goldsmiths* 11 (The Worshipful Company of Goldsmiths, 1984).
10. Diane Egbert, "Reticulation and Heat Coloration of Shakudo and Shibuichi," *Metalsmith* (Fall 1984): 38-41.

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