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O'DUBHGHAILL, Coilin <<http://orcid.org/0000-0002-1278-3036>> and JONES, Alan Hywel

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JAPANESE IROGANE ALLOYS AND PATINATION – A STUDY OF PRODUCTION AND APPLICATION

Dr. Cóilín Ó Dubhghaill

Senior Research Fellow, Art and Design Research Centre

Dr. A. H. Jones

Senior Research Fellow, Materials and Engineering Research Institute
Sheffield Hallam University
Sheffield, UK

ABSTRACT

Japanese metalworkers use a wide range of irogane alloys (shakudo, shibuichi), which are colored with a single patination solution (niiro). This approach allows different alloys to be combined in one piece and patinated, producing a multi-colored piece of metalwork.

At present the production of irogane alloys and their patination is an unreliable process. This study aims to develop reliable alloy production and a safe, easy-to-use and repeatable patination process using standard ingredients available from chemical suppliers.

The study has examined the production of shakudo and shibuichi alloys, characterizing the alloys produced by casting into cloth molds in hot water, into steel molds, and produced using continuous casting. The influence of traditional polishing methods was assessed using surface texture (S_a) measurements. Traditional rokusho, an ingredient of the niiro solution, was analyzed by XRF and XRD. Niiro patinated surfaces on a range of alloys were examined using XRD and $L^*a^*b^*$ color measurements.

HISTORICAL BACKGROUND

It is unclear exactly when the development of the shakudo alloy took place. It seems possible that it was developed in Japan from yamagane, or unrefined copper, which naturally had other impurities such as arsenic and gold, and could be patinated to a dark brown color. Craddock and Giumlia-Mair suggest an alternative origin, describing alloys similar to shakudo in Egypt and Greece dating from the mid-second millennium BC, and the possible transfer of these alloys to Japan through India and China.¹ The name shakudo first appeared in Japanese archives in the Nara period (710-784)² while the oldest existing shakudo piece in Japan, dating from 1164, is a scripture box belonging to the Taira family, found in Itsukushima shrine in Hiroshima.³ Gowland refers to shibuichi sword furniture of the 17th century and a first official record of the shibuichi alloy dating from 1706, when it was used in the Government Mint for the preparation of low silver content bars.⁴

sharpness when casting and to facilitate the production of a dark patina. An analysis of shiromi as published by William Gowland in 1894⁹ showed copper 72.70%, lead 8.53%, arsenic 11.37%, antimony 4.27%, tin 0.93%, iron 0.13 %, silver 1.33%, sulphur 0.33% and traces of gold. Shakudo alloys as used at Tokyo Geidai are shown in Table 1 below. The Geidai kuromido is listed as 97.1Cu2.9As.

Table 1 Geidai Shakudo

Geidai Shakudo	Best	3bu	2bu	1bu	grape	purple	purple	purple
Gold%	4.76	2.91	1.96	.098	0.5	13.04	16.67	23.08
Copper%	95.24	97.09	95.1	95.1	96.52	86.96	83.33	76.92
Kuromido%	0	0	2.94	2.94	2.99	0	0	0
Silver%	0	0	0	0.98	0	0	0	0

Shibuichi refers to a range of copper-silver alloys. Shibuichi literally translates as a quarter, a reference to the common alloy containing 25% silver. Shibuichi is also referred to as rogin (misty or hazy silver), aptly describing the quality and color of the surface patina. Shiro-shibuichi (white shibuichi) refers to an alloy with a high percentage of silver. Kuro-shibuichi (dark shibuichi) refers to a copper/silver/gold alloy. Shibuichi patinates to a range of colors from light grey to dark grey depending on the alloy. The eutectic structures formed in the alloy are responsible for the unique surface color and texture of shibuichi when patinated. Shibuichi alloys as used at Tokyo Geidai are shown in Table 2.

Table 2 Shibuichi alloys as used at Tokyo Geidai

Geidai Shibuichi	White Shibuichi	White Shibuichi	High Shibuichi	Average Shibuichi
Fine Silver%	60	50	40	25
Copper%	40	50	60	75

TRADITIONAL ALLOY CASTING: YUDOKOBUKI

In traditional Japanese metalwork, the alloys are cast into a cloth-covered mold in a hot water bath, rather than metal or stone molds. This technique is called yudokobuki (cloth mold casting). The alloy metals are melted together in a graphite crucible. The crucible is lined with a paste made from vegetable oil and rice bran, which acts as a reducing agent during the melting process. An additional flux is often added to the melt before pouring. The melted alloy is poured into a heavy cotton mold (sailcloth sewn into a copper frame), which is suspended in a hot water bath. The ingots cast by yudokobuki are then hammered to compress the crystalline structure of the metal. The ingot should be hammered from the outside edge inwards, starting first around the edges, and then hammering towards the center. This minimizes the chance of the edges splitting. Care should

Hughes and Rowe suggest that chemicals present in the daikon “may have the effect of acting as a mild surface activating agent, while the body of the paste may encourage a more even color by ensuring the initial coloring action is gradual” and also comment that the radish might act similarly to potassium bitartrate, which is used commercially in metal finishing as a ‘holding’ solution in which objects are kept immersed after cleaning and prior to coloring to prevent tarnish.¹²

Previous studies on Daikon, primarily to discern its health benefits, have indicated that it contains isothiocyanates.¹³ Other literature suggests that isothiocyanates are unstable and are precursors to the formation of thiourea.¹⁴ Thiourea is a well-known ingredient of some silver cleaning solutions where it is used to both clean and protect the silver surface.

Niiró solution

The ni-iro-eki (boiling-color-solution) is known by a number of names, including nikomi-chakushoku, ni-age, and ni-iro. In the West it has often been referred to as rokusho, one of its principle ingredients.

Oguchi lists solutions from “Kinko Seisakuho” published by Tokyo Geidai Professor Shimizu in 1937.¹⁵ The solutions are very close to the formulas listed in subsequent metalwork technical manuals and were probably the source for these books.¹⁶ The main components of the solutions are rokusho and copper sulfate with a variety of additions including alum, rice vinegar, pickled plums and plum vinegar. Oguchi achieved best success coloring copper to a bright red/brown color using a solution with addition of plum vinegar (up to 5ml per liter). In this study we use a solution of 5g rokusho, 5g copper sulfate and 5ml plum vinegar as a standard solution, having previously used this with success for studio work. Our aim is to find a solution that will produce a good red/brown on copper, even grey tones on shibuichi, a black or blue/black on shakudo and an even white color on fine silver.

Rokusho is an artificial verdegriis that was traditionally produced in Japan by the application of vinegar on copper sheet.¹⁷ It is commonly used in traditional Japanese painting as a pigment. Notis identifies rokusho as basic copper acetate $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{Cu}(\text{OH})_2$.¹⁸ Pijanowski suggests a method of producing rokusho from copper acetate, calcium carbonate and sodium hydroxide.¹⁹ The rokusho used for this study was “Genkyo brand best powdered pigment rokusho,” a popular brand among metalsmiths.

Plum vinegar is a by-product of the production of umeboshi pickled plums. The vinegar contains citric acid and a high salt content. The plum vinegar used for tests was produced by Chinriu Japan, with ingredients listed as plums and salt.

The niiró solution is heated in a copper or glass container. Distilled or filtered water should be used. The solution is boiled once to dissolve the ingredients. As water evaporates during the process, the container should be refilled to the original level. The workpiece is carefully suspended in the solution. This is commonly done using a copper, plastic or wooden support or a bamboo basket. Surfaces in contact with the workpiece are wrapped with cotton to prevent the

There is no standard practice with regard to the temperature of the niiro solution, with craftspeople and researchers using temperatures from body temperature up to boiling point. Lower temperatures (40°C/104°F) are usually recommended for the patination of shibuichi and brass.

MICROSTRUCTURES OF THE COLORED LAYER

Most of the published research in this area has focused on the shakudo alloy with a small amount of work on shibuichi, copper and brass.²⁰ Recent work by Kitada et al. provides useful information on microstructures. A study of niiro patinated copper showed that the surface consisted of a double layer chemically, a thin upper layer of copper (II) oxide such as CuO and an under layer of copper (I) oxide such as Cu₂O.²¹ The colored layer in shakudo was described as crystalline and amorphous Cu₂O with a crystal size of 30-80nm. Fine Au particles with 2-5nm diameters are distributed in the Cu₂O layer. The coloring is mainly due to light absorption and reflection by the fine Au particles distributed in the Cu₂O layer.²² A study of a 20%Ag shibuichi alloy found that the colored layer consisted of crystalline and amorphous Cu₂O and Ag nanograins of various shapes distributed in the Cu₂O matrix.²³

Workshop techniques

Three casting techniques were compared for the production of our candidate alloys: continuous casting, casting into a steel mold, and casting into a cloth mold in hot water. The alloys were cast from 99.99 Au and Ag and oxygen-free copper (CW008/C103), and best practice for workshop casting was followed.²⁴ In this study we have focused on the production of three alloys: 98Cu2Au shakudo, 50Ag50Cu shibuichi and a 75Cu25Ag shibuichi.

Continuous casting

Alloys were cast using an Indutherm CC 1000 machine at Capella Manufacturing Ltd, UK, melting under argon atmosphere at a temperature of 1100°C (2012°F). The alloys were subsequently cleaned in a 10% sulfuric bath and rolled, annealing at 650°C (1202°F) in a nitrogen atmosphere between stages.

Steel Mold casting

The shibuichi alloys were melted in a small induction furnace, the shakudo alloy was melted in a resistance furnace, both at a superheat of 100°C (180°F) over liquidus. 500g ingots of all alloys were produced. The shakudo alloy was stirred with a graphite rod during the melting process. The melt was covered with graphite chunks and poured into a lightly oiled steel mold heated to a temperature of 100°C (212°F). The surface of the ingots was milled clean. The ingots were then hammer forged before torch annealing to a dull red heat and quenching in cold water. The ingots were cleaned in a 10% sulfuric bath and then rolled, torch annealing between stages.

Water casting

The alloys were melted as described for steel mold casting. They were then poured into a cotton mold in the hot water bath. The water was heated to a temperature of 70°C (158°F), the thick sailcloth cotton mold was at a depth of 9cm. The water was agitated before and during pouring and solidification. Any irregularities on the surface of the ingots were ground back to clean metal. The ingots were hammer forged twice before rolling. The ingots were torch annealed to a dull red heat, and cleaned in a 10% sulfuric bath between stages.

Polishing technique

The samples for patination were polished with magnolia charcoal, paulownia charcoal, pumice and finally silicon carbide (1200 grit). Magnolia and paulownia charcoal blocks were dipped in water and rubbed on the metal. The pumice and silicon carbide were mixed into a paste with water and rubbed on the metal with a cotton cloth using a linear motion. The samples were then cleaned with sodium bicarbonate and water to remove traces of the polishing media.

Patination technique

After polishing, the test pieces were dipped in a 10% sulfuric acid/H₂O bath and then rinsed in H₂O before immersion in the niiro solution. Pieces that were being tested with daikon were dipped in the grated daikon immediately prior to immersion in the niiro solution. The test pieces were suspended from copper wire in the glass vessel. The solution was constantly agitated with an auto stirrer. After patination the test pieces were rinsed in water and then dried using hot air and cotton wool to prevent the formation of tide marks.

LABORATORY TECHNIQUES

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to observe the microstructures of the alloys and the appearance of the niir surfaces. Quantitative elemental analysis of the regions of interest was carried out using energy dispersive x-ray analysis. SEM was carried out using an FEI XL30 ESEM instrument equipped with an Oxford Instruments INCA energy dispersive x-ray analyzer (EDX). Imaging was primarily conducted in back scattered electron (BSE) mode, which provides contrast based upon the average atomic number and thus gives good contrast between the phases in the microstructure. EDX was used on the microstructures to quantify the composition of the phases present. On the niir surface EDX was used to measure the elements present at the surface of the patinated alloys.

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 radiation.

XRD was used in the glancing angle configuration in order to identify the phases present at the surface of the experimental niir materials. In this configuration the incident x-rays were directed at the sample with an incident angle of 1° which makes the resulting diffraction pattern more sensitive to phases present only on the surface, e.g., surface oxides or sulfides etc.

X-ray Fluorescence

X-ray fluorescence (XRF) was used to quantitatively measure the elemental content of the traditional rokusho materials. XRF was carried out on a Philips MagixPro spectrometer. XRF has a sensitivity level of the order of ppm and was used in order to discern both the bulk composition and the low presence of any undesirable elements such as lead or arsenic. However, XRF cannot detect H, C, O and N directly and in order to determine the copper acetate content, a series of tests were carried out after drying (120°C/248°F) and burn-off (600°C/1112°F) in which the weight losses were recorded in order to determine the volatile/organic content of the rokusho. The composition of the rokusho was estimated from a combination of the weight loss data and the XRF composition.

Casting Quality

Three casting techniques were used to produce the three alloys. The quality of the castings was assessed in several ways, including ingot shape (and suitability for subsequent rolling), surface finish and color (an indication of surface

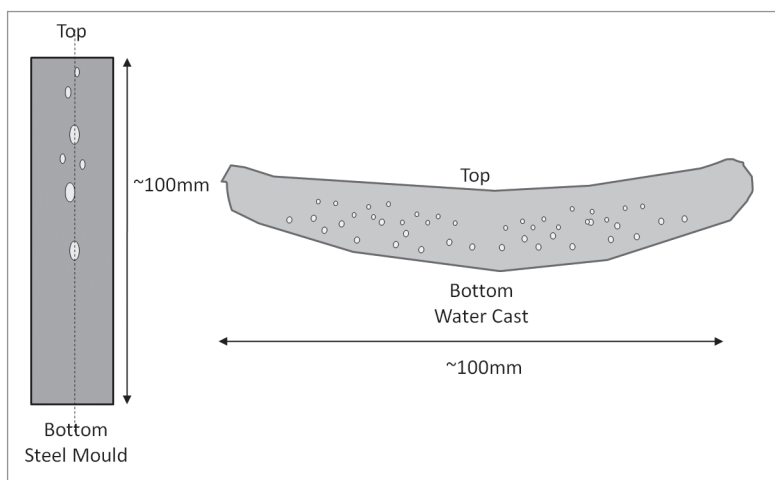


Figure 1 Schematic showing the approximate position and relative size of porosity observed in the workshop cast materials

Microstructure

The microstructures as recorded using SEM in atomic number contrast mode are shown in Figures 2, 3 and 4. For the shibuichi (Ag-Cu) alloys the microstructures are shown at low and high magnifications.

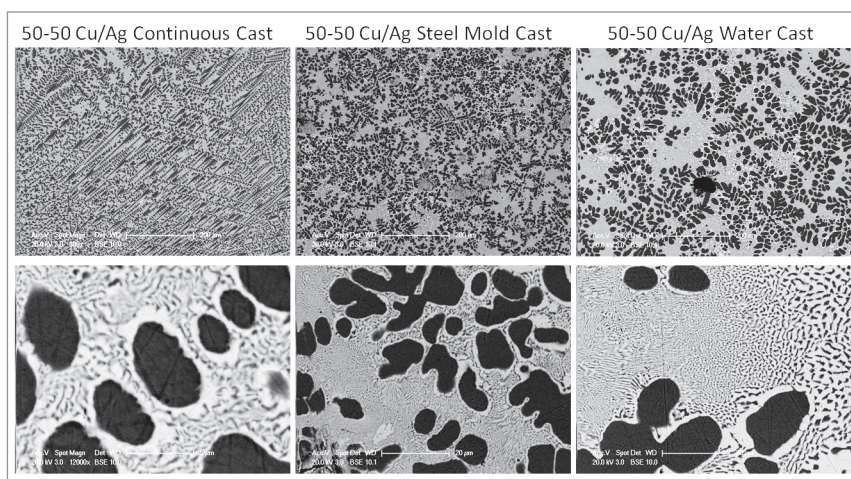


Figure 2 SEM images of the microstructure of 50-50 shibuichi alloys cast by different methods (top row = low magnification, bottom row = high magnification)

Cu-2%Au Water cast

25-75 water cast

50-50 steel cast

Typical porosity is shown in Figure 6. Spherical pores are most likely caused by gas porosity, while non-spherical porosity is more likely to be shrinkage porosity.

Rolling had a significant effect on the microstructure as is shown in Figure 7. In terms of the influence such a rolled structure may have on the appearance of niir, the elongation of both phases in the Ag-Cu alloys will make the apparent surface size of a Cu-rich grain or a eutectic region larger and thus potentially more visible to the naked eye when compared with the relatively small as-cast structure.

2. Magnolia charcoal block - paulownia charcoal block - pumice - paulownia (powdered) - tonoko - tsunoko. $S_a=65\text{nm}$

SiC appears to be a good final finish material but there seems to be a contradiction between the above result and those given in Table 4 and Table 5. Tsunoko also appears to produce a less effective polish when used in sequence than when used singly.

It was noted that the surfaces of the SiC-polished materials appeared to have SiC particles embedded in the surface. This was later confirmed using SEM and EDX, which detected significant amount of Si present on the SiC-polished surfaces. SiC is a particularly aggressive abrasive due to its extreme hardness (HV~2500-3000) and angular morphology. When used on soft substrates it can have a tendency to embed in the material being polished, and it is then difficult to remove. Embedded SiC can significantly affect the result for surface texture (S_a) as the particles stand proud of the surface or, if removed, form small craters. Variations in the hardness of the copper sheet and the pressure applied during hand polishing can lead to different levels of SiC being embedded and thus a different result for S_a . For example, in this study values of S_a when using SiC on copper have been observed between 50 and 130nm.

Rokusho Analysis

Samples of rokusho obtained from Japan were analyzed using XRF and XRD. The weight loss of the sample at 120°C (248°F) and 600°C (1112°F) in air was 10 wt.% and 50 wt.%, respectively. This was taken to mean that the samples contained ~10 wt.% H₂O and that at 600°C (1112°F) the weight loss was due to the burning off of the acetate portion ((CH₃OO)₂) of the copper acetate. XRF analysis resulted in the composition given in Table 6.

Table 6 Quantified elemental content of rokusho from XRF

Element	Mass%	±
Cu	32.2	0.1
Ca	26.8	0.2
Cl	18.9	0.2
Na	10.7	0.3
Zn	6.0	0.1
Pb	1.7	0.1
Sn	1.5	0.1
P	0.4	0.01
As	0.3	0.1
K	0.3	0.1
Si	0.3	0.01
Mg	0.14	0.01
Sb	0.14	0.03
Ni	0.14	0.01
Fe	0.13	0.01
Al	0.10	0.01
Other	0.25	-

X-ray Diffraction (XRD) of the green rokusho material revealed that the primary crystalline phases present were calcium carbonate (CaCO_3) and sodium chloride (NaCl). Any copper acetate that was present must have been present in the amorphous state as it was not detected by XRD. “There is broad hump at $\sim 17^\circ 2\theta$ ”, which may be the copper acetate, but the XRD database could not identify it.

Assuming that the copper acetate was present as the hydrated form $\text{Cu}(\text{CH}_3\text{OO})_2 \cdot \text{H}_2\text{O}$ and that all the acetate had burnt off at 600°C (1112°F), then the composition for rokusho given in Table 7 was obtained (considering only constituents present above 1 wt.%).

Table 7 Calculated rokusho composition

Compound	mass %	mass % (no Zn, Pb or Sn)
$\text{Cu}(\text{CH}_3\text{OO})_2 \cdot \text{H}_2\text{O}$	55%	53%
CaCO_3	34%	33%
NaCl	14%	13%
ZnO	4%	
PbO	1%	
SnO_2	1%	

NIIRO RESULTS

XRD results

Glancing Angle XRD was used to determine the phases which were present on the surface of alloys subject to niiro patination and using various niiro solutions and conditions.

Solution #1: 5g Rokusho/5g CuSO₄/1l H₂O

In this solution, which used the traditional Japanese sourced rokusho and omitted the plum vinegar, pure copper (sample C1) exhibited a strong signal from Cu_2O (cuprite). Shakudo (98Cu2Au) also exhibited a strong signal from Cu_2O . The XRD traces are shown in Figure 9.

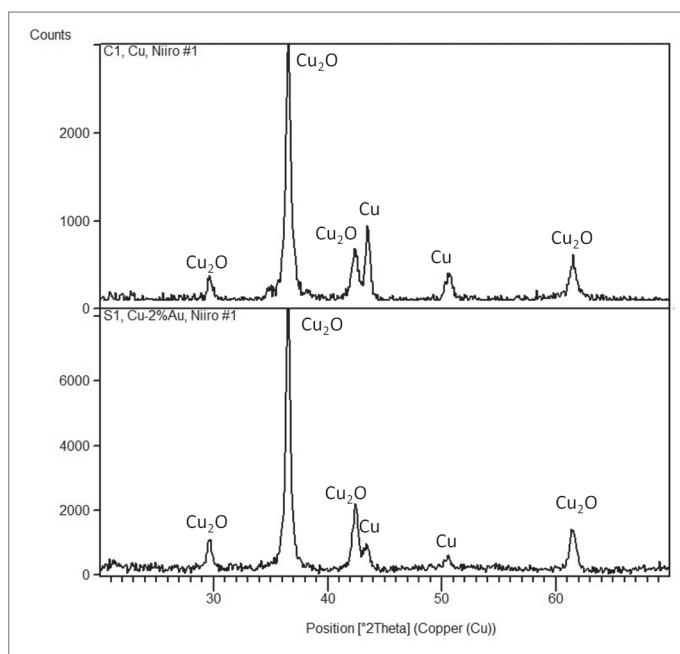


Figure 9 The glancing angle XRD trace from copper (C1, top) and shakudo (S1, bottom) patinated in Niirō #1 showing the formation of cuprite (Cu_2O)

The 50-50 Ag-Cu alloy (F3) subject to the same solution exhibited strong signals from Ag (actually the Ag-rich phase in the alloy) and Cu₂O. A 25-75 Ag-Cu alloy (T3) treated using this solution also exhibited Ag, Cu₂O and Cu from the substrate as shown in Figure 10.

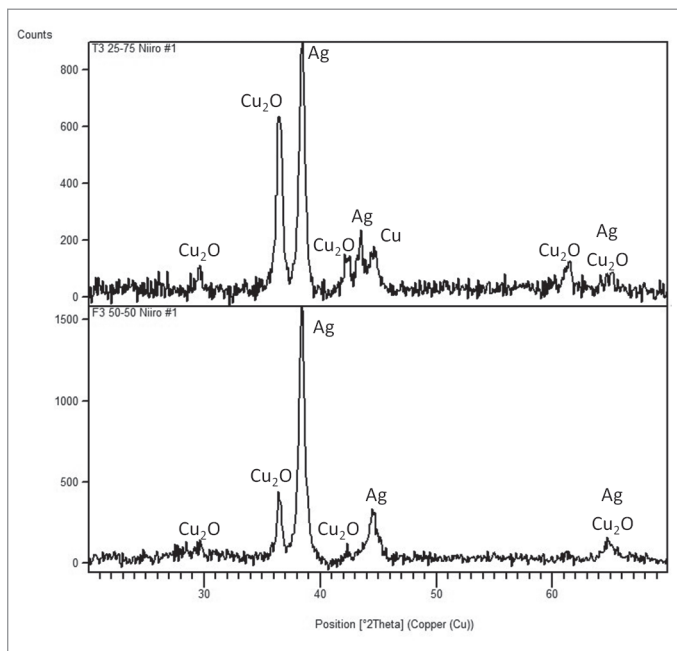


Figure 10 The glancing angle XRD trace from 50-50 shibuichi and 25-75 shibuichi patinated in Niiró #1

Solution #2: 5g Rokusho/5g CuSO₄/5ml Plum Vinegar/1l H₂O

In solution #2 the plum vinegar was added at ~5ml per 1l H₂O. The effect on the surface composition of the alloys was marked. On pure copper there was a strong signal from Cu₂O but also a significant signal from CuCl as shown in Figure 11. Similarly for shakudo (98Cu2Au, sample S3), a strong Cu₂O signal was accompanied by CuCl. Fine silver (Ag1) subject to solution #2 turned a light brown color, and the XRD results show that a significant layer of AgCl had formed on the surface as shown in Figure 12.

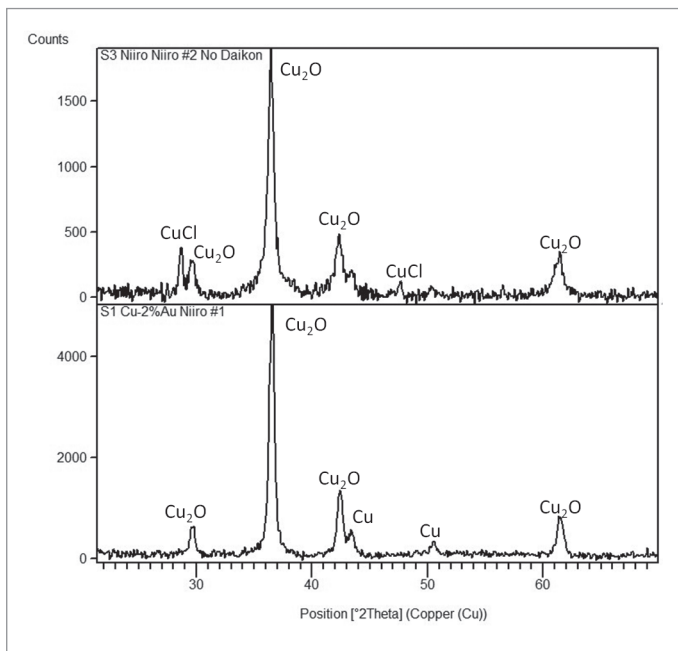


Figure 11 The glancing angle XRD trace comparing shakudo patinated using Niiro #2 (S3) with Niiro #1 (S1) showing the formation of CuCl in the case of Niiro #2

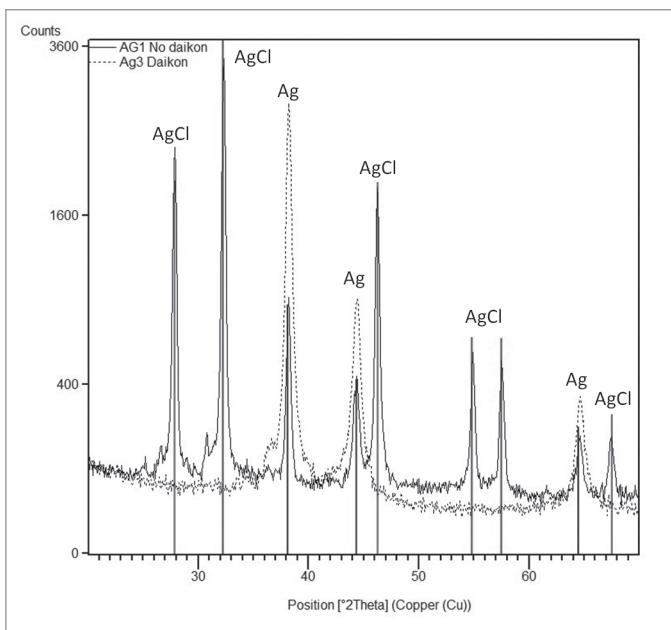


Figure 12 The glancing angle XRD traces for fine silver patinated in Niiro #2 with (Ag3) and without (Ag1) a daikon pre-treatment showing the formation of AgCl

A piece of copper niiro material that had been produced in Japan about 2001 with a deep and pleasing red/brown color was analyzed using glancing angle XRD as a comparative measure. The sample surface exhibited a strong signal from cuprite (Cu_2O) with a low signal from the Cu-based substrate.

Effect of Daikon

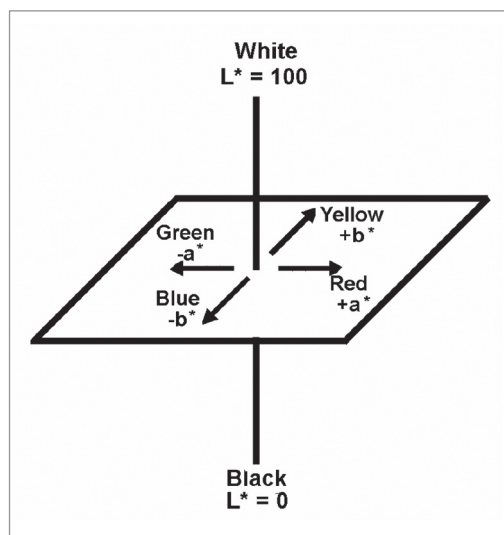
The effect of using daikon on fine silver can be clearly seen in the XRD results as shown in Figure 12. Sample Ag3 was treated with daikon before immersion in Niir #2, while Sample Ag1 was not treated with daikon and subject to the same immersion. The peaks for AgCl are clearly absent from the trace for Ag3.

It is clear from the glancing angle XRD results that the reactions that take place at the alloy surface are based on either the formation of copper oxide (Cu_2O) or the formation of copper oxide plus a chloride (CuCl). It appears that when only an oxide layer is present, it is the copper portion of the alloy (in the case of the shibuichi alloys) that reacts, while the silver layer does not form an oxide. When the chloride-forming reaction occurs, then both AgCl and CuCl can form. The presence of a chloride in the surface layers of niiro has not been reported extensively in the literature and in this instance appears to be related to the addition of the plum vinegar. The reason for the chloride formation is unclear but since the plum vinegar contains citric acid and added salt, it could be that a combination of additional chloride plus a change in the acidity of the solution may be responsible for the chloride formation. The formation of silver chloride appears to be suppressed by the use of daikon.

Color Measurements

The use of the Minolta Colorimeter allowed the objective measurement of the color of the niiro patinations. As the niiro solution was modified the effects on the color were recorded and quantified. Comparison was made between subjectively judged 'good' and 'bad' outcomes. The effect of using daikon was also measured.

The results from the Minolta CM508D 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 green. Similarly for the b^* axis, positive numbers tend towards the yellow and negative values towards blue. L^* varies between 0 and 100, where 0 is no light reflected (black) and 100 is total reflection (diffuse white). A schematic of the color space is shown in Figure 13.



*Figure 13 A schematic of the $L^*a^*b^*$ color space*

In order to simplify the graphical representation of the color of the samples, a two-dimensional plot was used with the x-axis representing the a^* value and the y-axis the b^* value. The L^* value was represented by the diameter of the data point and, for clarity, was also listed next to the data point. Differences in color can therefore be represented by the x-y position on the graph.

In the following figures the data points are labeled using the following format: "A,B, (C), D" where A = sample ID, B = the alloy (e.g., Ag, Cu, 98Cu2Au, 50-50, 25-75), (C) is the niiro solution # and D = the L^* value for that point. Where daikon was used this is also noted in the label.

The data on which the graphs are based are given in Table 9.

Table 9 Color measurement data for the various alloys and niiro solutions

Material	Sample	Niiro Solution	Time (mins)	Daikon (Y/N)	a*	b*	L*
Fine Silver	Ag1	2	30	N	7.3	14.5	60.0
	Ag2	2	30	Y	1.7	12.9	83.0
	Ag3	2	30	Y	2.3	17.2	81.0
	Ag4	2	30	N	8.5	14.8	60.0
Copper	C1	1	60	N	9.5	8.3	47.0
	C3	2	60	N	16.2	19.6	51.0
	C5	2	90	N	18.5	16.7	49.0
	C6	2	120	N	14.9	14.1	49.0
	C10	2	180	N	15.6	15.4	52.0
	C14 (2001)	-	-	-	14.8	8.1	36.0
	C15	4	120	N	31.3	24.8	46.0
	X1	2	120	N	21.5	15.6	48.0
Shakudo	S1	1	60	N	-0.2	-4.7	46.0
	S3	2	60	N	0.1	-3.9	43.0
	S6	4	120	N	3.5	-6.0	47.0
Shibuichi 25-75	T1	1	30	N	2.1	5.8	43.0
	T3	1	30	Y	2.8	7.6	49.0
	T2	2	30	N	3.1	9.7	53.0
	T4	2	30	Y	3.7	12.3	53.0
	T-X3	1	120	Y	0.9	4.0	55.9
Shibuichi 50-50	F1	1	30	N	3.7	14.5	54.0
	F2	2	30	N	2.1	12.0	55.0
	F3	1	30	Y	2.9	9.8	56.0
	F4	2	30	Y	3.2	14.4	59.0
	F-X3	2	120	Y	1.7	7.3	67.1

Figure 1 is an achromaticity (a^*) vs. chromaticity (b^*) diagram. The x-axis represents a^* (Redder) and the y-axis represents b^* (Yellower). The diagram shows color differences between various samples, plotted as circles. The samples are labeled as follows:

- Ag2, Fine Silver, (2), Daitkon, 83
- Ag1, Fine Silver, (2), 60
- Niir Soln #1
- C1, Cu, (1), 47
- C14, Japanese Cu Niir 2001, 36
- C6, Cu, 120m (2), 49
- C10, Cu, 180m (2), 52
- C3, Cu, 60m (2), 51
- Niir Soln #2
- C5, Cu, 90m (2), 49
- X1 Cu, (2), 48
- C15, Cu, 120m (4), 46
- Niir Soln #4

A dashed line connects points C3, C5, X1, and C6. A solid line connects points C1, C14, and C6. A solid line also connects points C10, C6, and C3.

Figure 14 shows the data for both fine silver and several pure copper samples. For fine silver there is a significant difference in the color produced when the piece is treated with daikon prior to immersion in the niiro solution. When daikon is used prior to immersion in niiro the piece is brighter ($L^*_{\text{daikon}} = 83$ compared with $L^*_{\text{no-daikon}} = 60$) and b^* is reduced by 2 and a^* by ~6.

The copper alloys patinated using Niir #2 had higher a^* and b^* values, suggesting a paler orange color (increased red and yellow). There does not appear to be a systematic change in color with time of immersion between 60 (C3) and 180 minutes (C10). Time alone does not appear to result in deeper reds, e.g., C6 and C10.

Sample X1, which was a pure Cu piece welded to the other alloys in a strip and immersed in Niiro #2 for 120 minutes, was judged to be a 'good red' color.

Patination of copper using Niiro #3, #5 and #6 was judged by eye to produce poor colors. Niiro #3 on copper produced poor dull brown colors with a low red value ($L^*=50$, $a^*=8$, $b^*=12$). XRD and SEM/EDX of these surfaces showed only Cu_2O present but it was seen to be present as very large crystals compared with those formed in other niiro solutions.

Sample C15 (Niiro #4, 120 minutes) was judged by eye to be a good red/brown color and was one of the brightest colors achieved. The very high a^* (red) value confirms that it is the reddest of the samples in this group. Niiro #4 was produced using laboratory-grade chemicals instead of traditional rokusho and included NaCl but not calcium carbonate or plum vinegar.

Shakudo

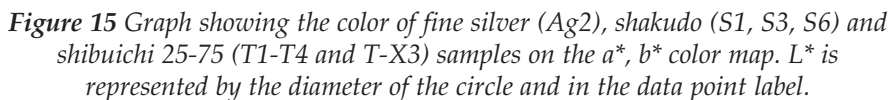
For shakudo ($98\text{Cu}2\text{Au}$) the color developed was significantly darker than the pure copper samples. To the naked eye the color was almost a dark blue/black, and this is confirmed by the negative b^* value (b^* was generally in the range -4 to -6 for these alloys) as shown in Figure 15. The values for a^* were mostly around 0 for Niiro #1 and Niiro #2 but $a^* \sim 3.5$ for Niiro #4. The difference between Niiro #1 and Niiro #2 was small but consisted of a small increase in a^* , i.e., more red, and a less negative value of b^* , i.e., less blue.

As for copper, patination of shakudo using Niiro #3, #5 and #6 produced poor colors. Using Niiro #3 (only copper acetate and copper sulfate) resulted in poor brown colors, which were streaky in nature ($L^*=44$, $a^*=5.5$, $b^*=1.2$).

However, Niiro #4, made from laboratory-grade chemicals and including NaCl, produced a pleasing blue/black color (S6), and it can be seen that its high a^* (red) value makes it a more blue color than S1 and S3.

Shibuichi

For 25-75 shibuichi and 50-50 shibuichi alloys (Ag-Cu) the results are shown in Figure 15 and Figure 16. In these graphs the data for niiro fine silver (using daikon, Ag2) are included for comparison. All the alloys showed values that were much closer to the fine silver niiro result (Ag2) than for the copper niiro result, e.g., C15 in Figure 14.



For 25-75 Ag-Cu alloys there is a significant difference in color between the use of Niiro #1 and Niiro #2. Niiro #1 generally produced a less yellow alloy (lower b^*) than Niiro #2. Sample T-X3, where the shibuichi was welded to other alloys in a strip, was considered to be the best sample with a clean grey color (not yellow or brown). Unlike fine silver, where the use of daikon reduced both the a^* and b^* values, here the use of daikon appeared to produce an increase in a^* (red) and b^* (yellow). Arrows in the figure indicate the color shift from daikon to no daikon.

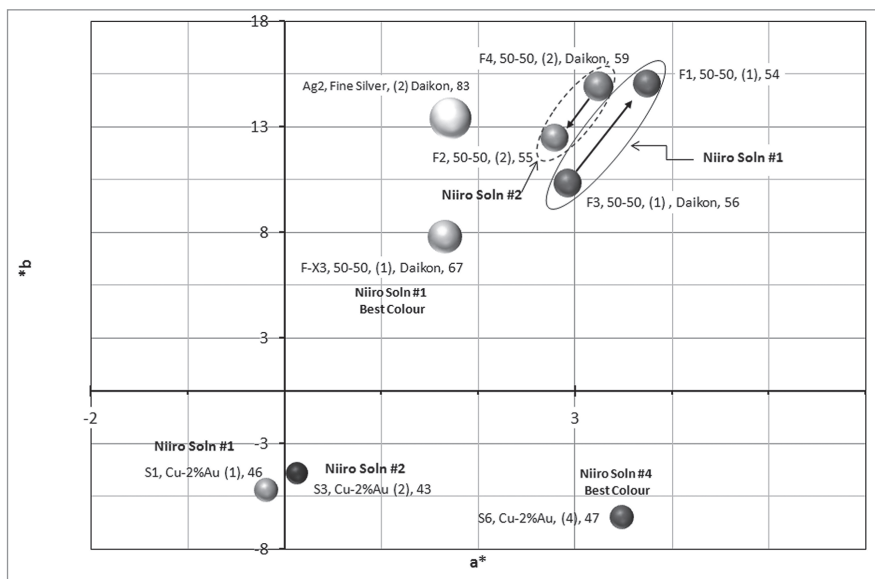


Figure 16 Graph showing the color of fine silver (Ag2), shakudo (S1, S3, S6) and shibuichi 50-50 (F1-F4, F-X3) samples on the a^* , b^* color map. L^* is represented by the diameter of the circle and in the data point label.

For 50-50 Ag-Cu alloys there was very little difference between the use of Niiro #1 and Niiro #2. The effect of daikon in Niiro #1 was to reduce a^* and b^* (as seen for fine silver) but for Niiro #2 the opposite was true (increased a^* and b^*), as indicated by the direction of the arrows on the graph. Sample F-X3, where the shibuichi was welded to other alloys in a strip, was considered to be the best sample with a clean grey color (not yellow or brown).

Correlation between Color and Surface Composition

The results from the glancing angle XRD results indicate that in the case of Niiro #1, only Cu_2O is formed on the surface of the alloys. Ag does not appear to react with Niiro #1. However, under the conditions used here Niiro #1 did not produce 'good' colors on copper. Even though it contains NaCl, no chloride-forming reaction was active in Niiro #1.

When using Niiro #2 (with added plum vinegar), XRD detected significant chloride formation. Fine silver not treated with daikon produced silver chloride (AgCl), which was light brown in visual appearance and is seen in the color results as a significant shift in the a^* value towards the red and a large drop in L^* , e.g., Ag1 in Figure 14.

On copper-containing alloys patinated with Niiro #2, copper chloride (CuCl) was also observed, and the color change caused by the chloride consisted of an increase in a^* (red) and b^* (yellow), which was more marked on the pure copper than on the shakudo. Under the conditions used here, Niiro #2 did not produce the best colors but some were acceptable, e.g., copper X1 and shakudo S3.

COLOR RESULTS AND SURFACE COMPOSITION.

Extensive patination trials on copper, shakudo, and the two shibuichi alloys have been carried out in workshop conditions.

When traditional niiro compositions are used without the addition of plum vinegar, the surfaces of copper-containing alloys develop a thin layer of Cu_2O (cuprite). There was no systematic change in color with increasing immersion time (60 to 180 minutes) on copper.

Colors achieved on copper using niiro with plum vinegar were regarded as preferable in terms of their aesthetic appearance and comparison with other traditional Japanese work, one piece of which was measured here.

The addition of plum vinegar to niiro has a significant effect on the surface composition, with both copper and silver chlorides present in significant amounts. The presence of chlorides has a large effect on the colors, generally adding a browner tinge to the patination of fine silver and shibuichi alloys, which is not desirable.

Shibuichi niiro colors are always closer to the color of fine silver niiro despite 25 to 50% of the alloy being copper. The shibuichi surfaces develop either Cu_2O or ($\text{Cu}_2\text{O} + \text{CuCl}/\text{AgCl}$) and are never observed to form silver oxides.

On fine silver a light brown silver chloride layer is formed. However, if the piece is rubbed with grated daikon prior to immersion, then the formation of silver chloride is virtually eliminated. It appears that the daikon is acting as an inhibitor to the formation of silver chlorides while leaving the copper still able to oxidize. It probably has little effect on copper or shakudo. Work is under way to determine if thiourea could be a suitable substitute for daikon in this work.

Niiro solutions made up from laboratory-grade materials containing only copper acetate and copper sulfate did not produce acceptable colors on copper and shakudo. However, with Niiro #4 (which included NaCl), the good colors were produced on copper (red/brown) and on shakudo (blue/black). These colors have been quantified using the $L^*a^*b^*$ system for future reference.

CONCLUSIONS

- Continuous cast shakudo and shibuichi alloys offer an alternative to workshop cast materials without the inherent problems of workshop casting, i.e., porosity and problematic cast ingot shape.
- The final polish finish achievable using traditional materials such as tonoko and tsunoko can be replicated by the use of SiC grit 1200. However, the embedding of the SiC in the surface can give rise to variability in final finish. Alternative abrasives such as Al_2O_3 and SiO_2 should be considered as alternatives.
- Japanese rokusho has been found to contain copper acetate, sodium chloride (common salt) and calcium carbonate as its main constituents. The presence of salt and calcium carbonate has not been reported extensively in the previous literature on the subject.

- Lead, tin and zinc are also present in rokusho at significant levels, probably as a result of the use of brasses and/or bronzes in the production method. The presence of Pb (and other heavy metals) could be a barrier to the more widespread use of niiro in the West and the development of a 'safe' commercial-grade niiro is desirable.
- The application of grated daikon radish to the alloys before patination does not appear to encourage even patination growth. The daikon does, however, reduce the formation of silver chlorides on fine silver during niiro patination.
- A systematic method of recording and quantifying the colors produced by niiro patination has been developed and a database of alloys, niiro compositions, conditions of immersion and colors has been produced and will be used in further work and in the comparison with other research.
- The addition of plum vinegar to niiro with NaCl results in chlorides forming on the surfaces of fine silver and shibuichi alloys, to the detriment of the color.
- When using laboratory-grade niiro, the presence of NaCl was found to be necessary for the production of good colors. The best colors on copper (red/brown) and shakudo (blue/black) were produced using a niiro-containing laboratory-grade copper acetate, copper sulfate and sodium chloride with plum vinegar and calcium carbonate omitted.

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