

Japanese irogane alloys and patination – a study of production and application

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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 verdegris 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

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 Cu₂O (cuprite). Shakudo (98Cu2Au) also exhibited a strong signal from Cu₂O. The XRD traces are shown in Figure 9.

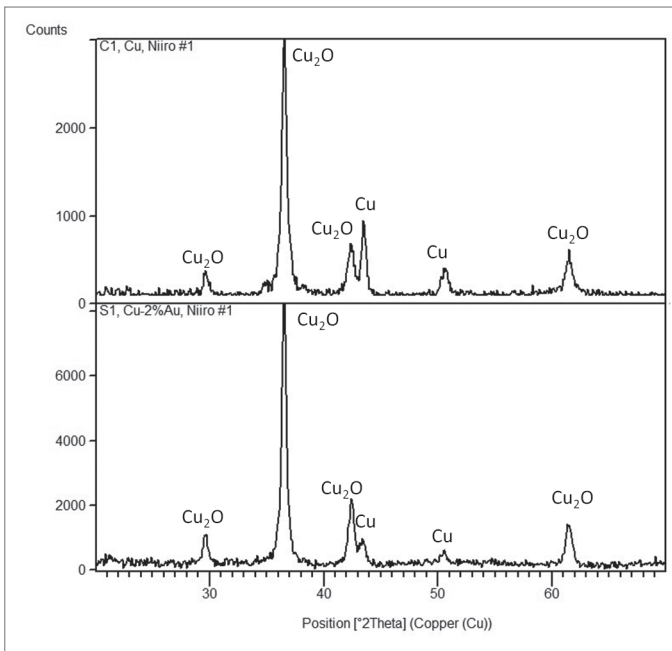


Figure 9 The glancing angle XRD trace from copper (C1, top) and shakudo (S1, bottom) patinated in Niirro #1 showing the formation of cuprite (Cu₂O)

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.

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 Niiro #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.

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 (98Cu2Au) 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.

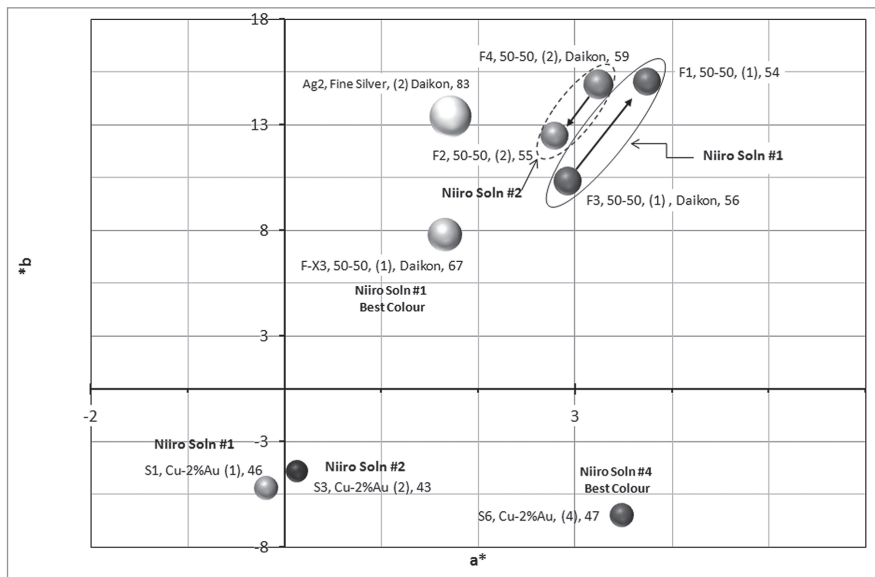


Figure 16 Graph showing the color of fine silver (Ag2), shakudo (S1, S3, S6) and shibuichi 50-50 (F1-F4, F-X3) samples on the a^* , b^* color map. L^* is represented by the diameter of the circle and in the data point label.

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.

