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Japanese Irogane Alloys and Patination – A Study of Production and Application

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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). 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]

Tracing the development of the niiro patination technique is more difficult. Oguchi writes that in Japan, the niiro patination technique is considered to have evolved around the late Heian Period (794-1185). The earliest extant objects colored with niiro are said to date from the later Muromachi period (1336-1573), while the earliest technical text describing the niiro technique is the Soken Kisho of 1781.[5]

The use of colored metal alloys came to great prominence in the sword furniture of Edo period Japan (1603-1868), from the somber shakudo work of the Goto family to the flamboyant inlays of the machibori artisans. The haitorei edict of 1876 banned the wearing of swords, causing the production of sword furniture to decrease dramatically. Japanese metalworkers found new outlets for their traditional techniques producing objet d'art, vases, and furniture for the rich merchants and the vast new export market. The ancient techniques soon spread to the West, with companies such as Christofle in France and Tiffany's and Gorham in the US quick to pick up on the possibility of the new alloys.[6] Use of the alloys has continued into the present day in Japan and on a smaller scale in the West for the production of jewelry and metalwork.

Metals and alloys used with Niiro patination

A wide range of pure metals and alloys can be patinated with the niiro solution – copper, shakudo (Cu/Au), shibuichi (Cu/Ag), kuromido (Cu/As), brass, and bronze, in combination with fine silver and gold (which retain their natural colors after patination). In this study we focus on the irogane (colored metal) alloys – shakudo and shibuichi in combination with copper and fine silver.

Shakudo is an alloy of copper and gold which patinates to colors ranging from brown to blue/black. Shakudo literally translates as red copper, possibly a reference to the color of the copper before patination. Shakudo is also sometimes referred to as crow or cormorant copper. A good shakudo patina is described as having a similar color to a 'wet crow's wing.' The classic rich black shakudo has a gold content of 3 to 5% gold. Lower gold content, from 0.25% to 3%, results in a range of brown to black colors. Silver and kuromido are sometimes used as alloying agents for low-grade shakudo. Shakudo alloys with a gold content of over 10% are referred to as budo-kin (grape gold) or shi-kin (purple gold).

The higher gold content alloys keep their color better over time: Nakatani reports that a 4.8% Au shakudo kept an attractive blue/black color better than lower gold content shakudo over an 11-year period. However, Nakatani also achieved a similar result by using a shakudo/kuromido alloy – 49.75Cu49.75kuromido 0.5Au. The kuromido contained 99.2Cu0.67As0.12Zn0.01Fe.[7]

Modern kuromido is usually an alloy of copper with arsenic (under 3%), which patinates from dark brown to black. Kuromido translates directly as 'black flavor copper.' The historic use of a copper/arsenic alloy in Japan is probably related to silver production byproducts. In the liquation process, unrefined copper is alloyed with lead to extract the silver from it.[8] If there was a high arsenic content in the copper, a byproduct called shiromi was also produced. Shiromi was used as an alloying ingredient to give additional hardness to alloys, to improve the sharpness when casting and to facilitate the production of a dark patina. An analysis of shiromi as published by William Gowland in 1894[9] 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 be taken to reduce the thickness of the center slowly, annealing often to allow the internal tensions in the metal to be released.[10]

The yudokobuki method is believed to give a better quality alloy than use of modern iron molds. Casting under hot water reduces the formation of surface oxides and slows down the cooling speed of the metal, which is believed to contribute to good working characteristics in the cast ingot.

Recent study by Sekii compared the casting of a shibuichi alloy (75Cu25Ag) and pure copper ingots using yudokobuki at different temperatures.[11] Sekii used a charcoal furnace with an electric blower. A graphite crucible was coated with a paste of vegetable oil and rice bran to enhance the reducing atmosphere. Sekii found that a water temperature of 45°C to 80°C (113ºF to 176ºF), with the surface of the cloth mold at a depth of 9cm, produced the best results. Sekii suggests that the slow cooling process in yudokobuki reduces internal shrinkage, producing ingots with less shrinkage porosity.

NIIRO PATINATION TECHNIQUE

Surface texture

The surface texture of the metal plays an important part in the final color of the metal. For example, rough surface texture, such as a textured hammer surface on copper, produces a dark brown color; planished surfaces on copper result in a brighter red-brown color whereas copper surfaces, which have been polished to a high finish, result in the brightest red-brown colors.

Polishing

Polishing of the alloys is crucial because of surface segregation during casting and surface enrichment during acid cleaning. The top surface layer of the metal is removed to expose the underlying alloy to patination.

Polishing can include initial polishing with grindstones and charcoal, finer polishing with pumice, powdered charcoal, clay powder (tonoko) and powdered calcined deer horn (tsunoko). The charcoal used for polishing is usually magnolia charcoal (rough) and paulownia charcoal (smoother). Tonoko is made from powdered burnt clay or pulverized whetstone and is traditionally used for polishing swords. The piece is finally cleaned with sodium bicarbonate before rinsing vigorously.

Daikon

Grated daikon radish is often applied to the surface of a piece after it has been cleaned and polished and just prior to immersion in the niiro solution. It is believed to prevent unevenness in the growth of the patina during the niiro coloring process, and to prevent fine silver from turning yellow in the solution. It is not understood exactly how the daikon helps in this process.

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.

Niiro 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 $Cu(C_2H_3O_2)_2 \cdot 2Cu(OH)_2$.[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 niiro 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 piece being scratched. Precipitation from the solution ingredients will form on the piece during the coloring process. To prevent this from causing uneven color development, the workpiece or solution should be agitated during the coloring process.

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/104ºF) 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 a CuO and an under layer of copper (I) oxide such as Cu_2O.[21] The colored layer in shakudo was described as crystalline and amorphous Cu_2O with a crystal size of 30-80nm. Fine Au particles with 2-5nm diameters are distributed in the Cu_2O layer. The coloring is mainly due to light absorption and reflection by the fine Au particles distributed in the Cu_2O layer.[22] A study of a 20%Ag shibuichi alloy found that the colored layer consisted of crystalline and amorphous Cu_2O and Ag nanograins of various shapes distributed in the Cu_2O 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 (2012ºF). The alloys were subsequently cleaned in a 10% sulfuric bath and rolled, annealing at 650°C (1202ºF) 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 (180ºF) 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 (212ºF). 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 (158ºF), 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/H_2O bath and then rinsed in H_2O 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 niiro 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 niiro 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 niiro 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/248ºF) and burn-off (600°C/1112ºF) 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 segregation), density (a measure of how much porosity is present), and porosity type and location. Small sections were taken from the ingots for density measurements using the Archimedes method. For workshop cast steel molds and water casting, a typical ingot was sectioned through its center line to assess the position and type of porosity.

Surface Finish Assessment

In order to assess and quantify the effect of the various polishing techniques on surface finish, Infinite Focus Microscopy (IFM) was used. The Alicona IFM measures the surface topography of the sample using non-contact, optical methods and provides a full-color 3D reconstruction of the surface. Using calibrated software allows the assessment of the surface roughness as measured over a defined area (S_a). S_a is defined as the average surface height of the area being measured. This is comparable to the more common R_a but uses an area rather than a linear scan and is more representative of the topography of large areas. Analysis was carried out using the x50 objective lens for all polishes.

Flat coupons of copper were polished using standard metallographic techniques to a final finish using 6μm diamond paste. The samples were then polished by hand using various traditional polishes and a linear motion. The resulting surface finish was measured in terms of surface roughness (S_a) using an Infinite Focus Microscope (IFM).

Mechanical Properties

The mechanical properties of each alloy were assessed using Vickers hardness measurements at a load of 10Kg. The influence of rolling and annealing on the hardness for each alloy was measured. A simple conversion to ultimate tensile strength was used to estimate the materials' expected strengths.

Results

Casting Quality

The continuous cast alloys were very easy to work, with no major flaws evident during the production of sheet. The steel mold and water cast ingots were much more problematic, with surface flaws, edge splitting and blistering evident during forging, rolling and annealing operations. Although the water cast ingots look aesthetically pleasing, with a smooth pebble form, the irregular cross section of the ingot (thick in the middle, thin at the edges) makes them particularly time consuming to hand forge to a point where they can be rolled in a mill.

The three alloys cast by continuous casting produced ingots with uniform dimensions. Density measurements of the alloys revealed that the continuous cast materials had achieved very close to theoretical density, which implied that there was very little, if any, porosity present. The density results for all alloys are given in Table 3.

The alloys cast in the workshop using steel molds showed good mold fill and hence the resulting ingot replicated the mold geometry. The density of the steel mold castings showed that there was porosity present at between 2% for 50-50 and 25-75 materials and 4% for 98Cu2Au. Sections through the ingots showed that the porosity was present along the center line of the casting and concentrated towards the top of the ingot. The pores appeared to be relatively large (0.5mm-2mm) and infrequent.

The shape of the water cast ingots was a 'pebble' shape with a smooth convex surface in contact with the muslin and a rougher top concave surface. They also exhibited lower than theoretical densities, which indicated porosity levels of ~2% for the 25-75 and 50-50 alloys and ~7% for the 98Cu2Au alloy. Sectioning of the ingots revealed more numerous pores with a much smaller size (max. ~0.5mm) than the steel mold cast material. The porosity was concentrated towards the top surface of the ingot.

Casting porosity can take two common forms: gas porosity, caused primarily by dissolved hydrogen in the molten metal escaping on cooling, or shrinkage porosity, where there is no available pool of liquid metal to fill a void formed by the shrinkage of the solidifying material. The basic melting methods and the turbulent nature of the metal pouring in both workshop techniques make it likely that there is a significant amount of dissolved gas in the molten metal. The relatively rapid cooling in both the workshop techniques also makes shrinkage porosity more probable.

In the continuous casting process the melt is purged with inert gas to prevent hydrogen solubility and hence minimize the chance of gas porosity. The solidification process is also well controlled and thus shrinkage porosity is also less likely.

Rolling (4x 25-50% reduction) with annealing between each step appeared to improve the density of the alloys, suggesting that the rolling process was compressing and eliminating the pores. However, it was clear that they were not completely eliminated in all cases as some rolled sheets exhibited bubbles or blisters after the annealing process. Such blisters are detrimental to the production of decorative work.

Work hardening of the alloys during rolling was significant as shown in Table 3. Annealing at 650°C (1202°F) in a reducing atmosphere of N_2 with 5% H_2 on a belt furnace for 30 minutes was sufficient to anneal the alloys fully.

***Table 3** The results from density measurements, porosity and hardness for the as-cast and rolled materials produced via different casting methods*

Condition	As Cast			Rolled		
Material	Density (g/cm^3)	Porosity %	Hardness HV10	Density (g/cm^3)	Porosity	Hardness HV10
Cu-2% Au As-Cast Continuous	8.99	0.1%	55	8.98	0.2%	130
Cu-2% Au As-Cast Workshop Steel Mold	8.61	4.3%	53	9.03	0.0%	-
Cu-2% Au As-Cast Workshop Water Mold	8.4	6.6%	55	9.04	0.0%	-
50-50 As-Cast Continuous	9.59	0.4%	96	9.61	0.2%	185
50-50 As-Cast Workshop Steel Mold	9.44	2.0%	98	9.61	0.2%	-
50-50 As-Cast Workshop Water Mold	9.48	1.6%	92	9.51	1.2%	-
25-75 As-Cast Continuous	9.201	0.6%	70	9.22	0.3%	170
25-75 As-Cast Workshop Steel Mold	9.08	1.9%	98	9.20	0.6%	-
25-75 As-Cast Workshop Water Mold	9.04	2.3%	68	9.31	0.0%	-

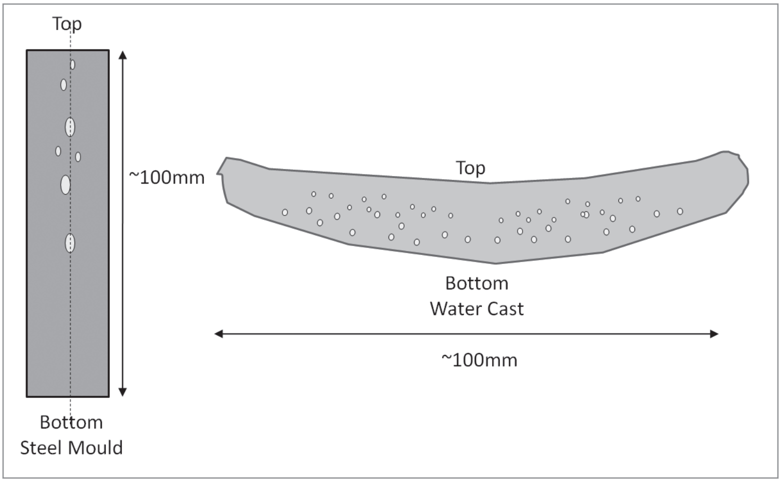

Figure 1 *Schematic showing the approximate position and relative size of porosity observed in the workshop cast materials*

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.

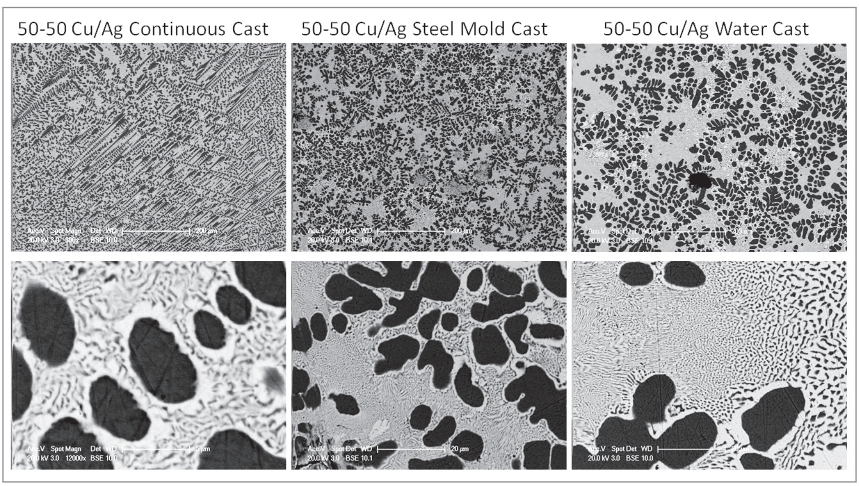

Figure 2 *SEM images of the microstructure of 50-50 shibuichi alloys cast by different methods (top row = low magnification, bottom row = high magnification)*

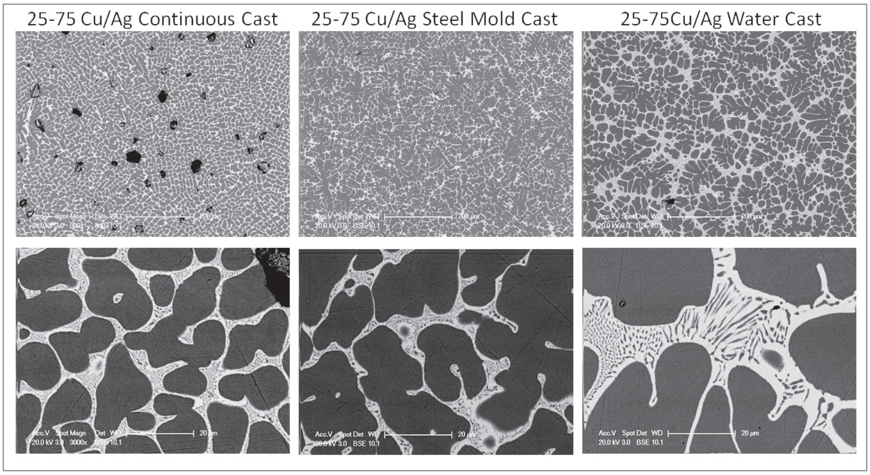

Figure 3 *SEM images of the microstructure of 25-75 shibuichi alloys cast by different methods (top row = low magnification, bottom row = high magnification)*

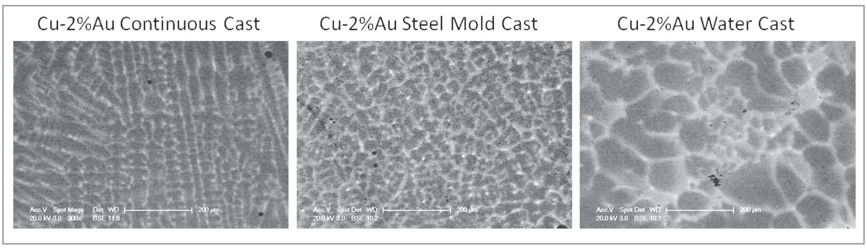

Figure 4 *SEM images of the microstructure of 98Cu2Au shakudo alloys produced via different casting methods*

The results show that the casting method can have a significant effect on the resultant microstructure. The differences are primarily a result of the cooling rate experienced by the alloys. There are clearly larger areas of eutectic phase present in the Ag-Cu water cast alloys. For the 98Cu2Au alloy the bright regions were shown to be rich in Au (at ~ 4 wt.%), and the slower cooling rate of the water cast alloy is apparent by the larger grains observed in this microstructure.

In both Ag-Cu alloys produced by continuous casting, there was evidence of a surface segregation effect where the top 10-20μm consisted almost entirely of the eutectic phase as shown in Figure 5. This layer will obviously need to be removed if it is to not affect the subsequent niiro process.

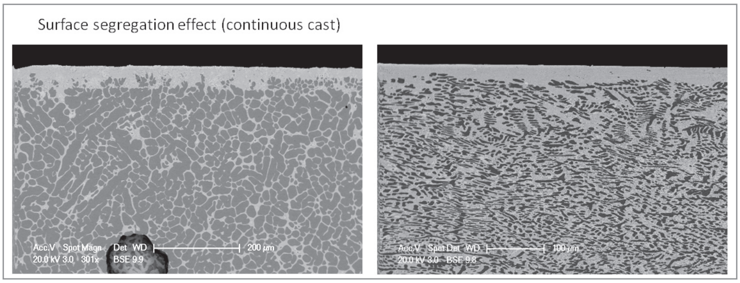

Figure 5 *Surface segregation of the eutectic phase in continuous cast shibuichi alloys (left = 50-50 Ag-Cu and right = 25-75 Ag-Cu)*

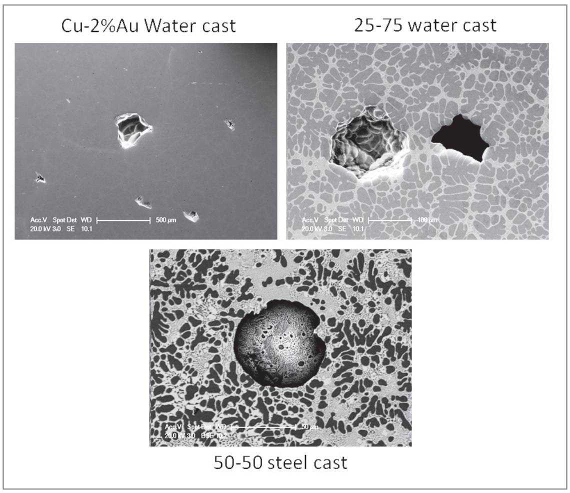

Figure 6 *SEM images of typical porosity found in workshop cast alloys (top left = shakudo, top right = 50-50 shibuichi, bottom = 25-75 shibuichi)*

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 niiro, 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.

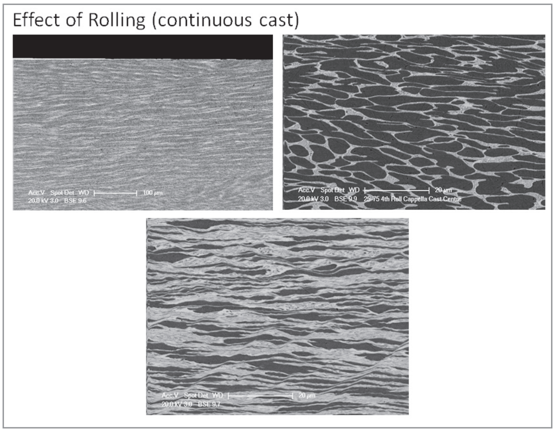

__Figure 7__ SEM images of the effect of rolling on the microstructure of continuous cast alloys (top left = shakudo, top right = 50-50 shibuichi, bottom = 25-75 shibuichi)

Surface Roughness of Polished Surfaces

The surface texture (S_a) data for the various polishing materials used singly on copper alloys are shown below in Table 4, and images of a selection of surfaces are shown in Figure 8. The results for copper plates, which were first planished using a polished hammer, are also shown in Table 5, but note that these results were achieved by using the polishes in sequence rather than singly.

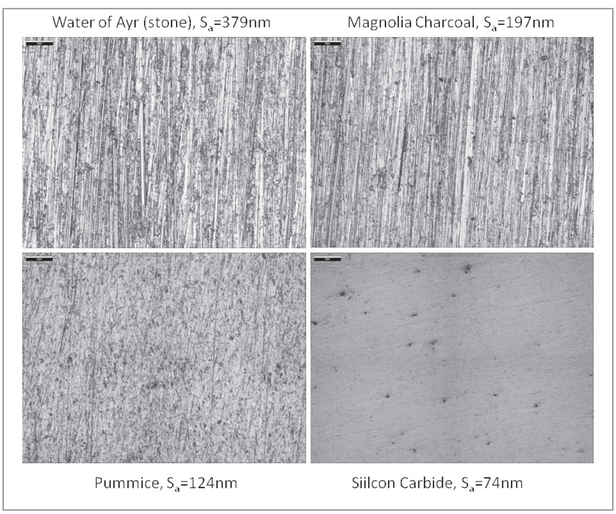

__Figure 8__ Optical microscopy images of the polished surface of copper samples after polishing with various polishing media

Table 4 *Surface Texture (S_a) measurements for each polishing media on laboratory polished copper*

Polishing Media	S_a (nm)
Lab Polished (6μm)	44
Water of Ayr (stone)	335
Magnolia Charcoal (block)	197
Paulownia Charcoal (block)	137
Pumice	124
Paulownia (powdered)	74
SiC (1200 grit)	97
Tonoko (clay)	46
Tsunoko (calcined deer antler)	12

Table 5 *Surface texture (S_a) measurements from planished samples polished in sequence*

Planished + Polished	S_a (nm)
As Planished	59
+Pumice	111
+Pumice + Bicarb	101
+Silicon Carbide (1200 grit)	99

The results show the ultimate surface texture achievable by the different polishing media when used singly (as opposed to sequentially). A very fine finish is achievable by using the traditional materials such as charcoal powder (paulownia), clay (tonoko) and calcined deer antler (tsunoko).

When used in sequence on a planished surface, the surface roughness tends to increase initially, suggesting that it may be better to start directly with the finer polish from the planished condition. However, this may not allow the "smoothing out" of various surface defects from planishing that is possible when using the coarser polishes.

In addition to the above measurements the surface texture of copper was measured after two sequences of polishing (listed below) in order to determine if SiC was a sufficiently fine final polish.

1. Magnolia charcoal block - paulownia charcoal block - pumice - SiC 1200. S_a=48nm

2. Magnolia charcoal block - paulownia charcoal block - pumice - paulownia (powdered) - tonoko - tsunoko. S_a=65nm

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 (248ºF) and 600°C (1112ºF) in air was 10 wt.% and 50 wt.%, respectively. This was taken to mean that the samples contained ~10 wt.% H_2O and that at 600°C (1112ºF) the weight loss was due to the burning off of the acetate portion ($(CH_3OO)_2$) 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 ~17° 2θ", 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 $Cu(CH_3OO)_2.H_2O$ and that all the acetate had burnt off at 600°C (1112ºF), 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)
$Cu(CH_3OO)_2.H_2O$	55%	53%
$CaCO_3$	34%	33%
NaCl	14%	13%
ZnO	4%	
PbO	1%	
SnO_2	1%	

Note that it was not known which Zn, Sn and Pb compounds were present and as such the presumption was made that they are present as oxides even though they may be other compounds such as acetates or chlorides (but not detected by XRD).

This result compares well with other reports in the literature for the composition of rokusho. It should be noted that the composition of the green rokusho powder sourced from Japan contain relatively high levels of Zn, Sn and Pb. This leads to the conclusion that the practice for producing rokusho involves the use of brasses and/or bronzes, which can be corroded using acetic acid to produce the green copper acetate. It is not known whether the $CaCO_3$ and NaCl constituents are added deliberately or are a consequence of the reaction used to produce the rokusho. In the limited number of prior studies of rokusho, there is only a passing mention of the presence of NaCl.

Niiro Solutions

Two traditional niiro solutions were prepared using the Japanese rokusho. Niiro #1 contained only rokusho (5g) and copper sulfate (5g) in 1l H_2O. Niiro #2 was identical but with the addition of 5ml of plum vinegar.

Simulated niiro solutions (#3, #4, #5 and #6) were based upon the composition measurements given above. Niiro #3 contained only the laboratory-grade copper acetate and copper sulfate. Niiro #4 had NaCl added, Niiro #5 had NaCl and $CaCO_3$ added and Niiro #6 had all these plus plum vinegar. The effect upon color of solutions #3, #4, #5 and #6 was only tested on the Cu and shakudo alloys. A list of the compositions used is given in Table 8.

***Table 8** Composition of the various niiro solutions used*

Niiro Solution #	Rokusho (g)	$CuSO_4$ (g)	Plum vinegar (ml)	Copper acetate (g)	NaCl (g)	$CaCO_3$ (g)	H_2O (l)
Solution #1	5	5					1
Solution #2	5	5	5				1
Solution #3		5		2.65			1
Solution #4		5		2.65	0.65		1
Solution #5		5		2.65	0.65	1.7	1
Solution #6		5	5	2.65	0.65	1.7	1

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 $CuSO_4$/1l H_2O

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.

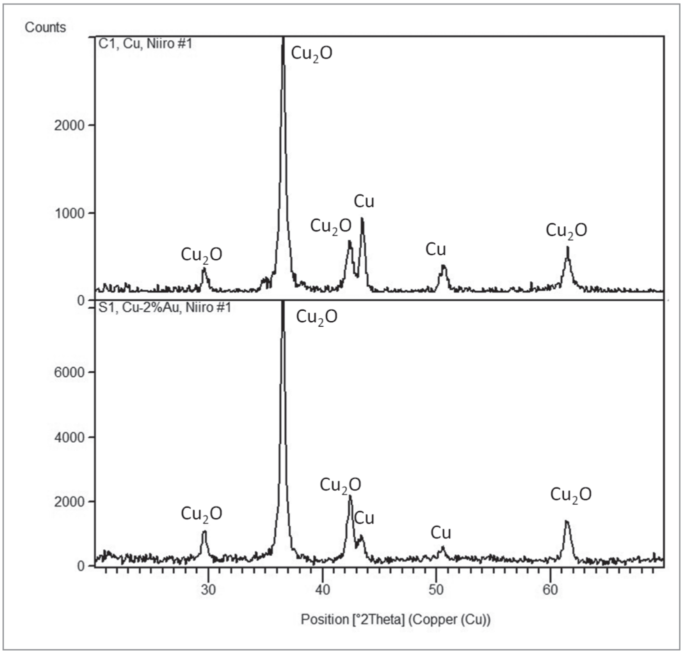

Figure 9 *The glancing angle XRD trace from copper (C1, top) and shakudo (S1, bottom) patinated in Niiro #1 showing the formation of cuprite (Cu_2O)*

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 Cu_2O. A 25-75 Ag-Cu alloy (T3) treated using this solution also exhibited Ag, Cu_2O and Cu from the substrate as shown in Figure 10.

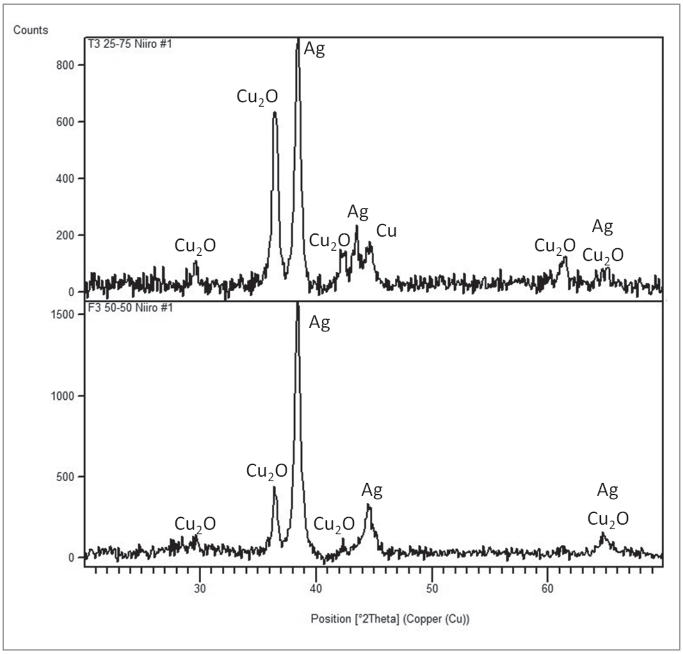

Figure 10 *The glancing angle XRD trace from 50-50 shibuichi and 25-75 shibuichi patinated in Niiro #1*

Solution #2: 5g Rokusho/5g $CuSO_4$/5ml Plum Vinegar/1l H_2O

In solution #2 the plum vinegar was added at ~5ml per 1l H_2O. The effect on the surface composition of the alloys was marked. On pure copper there was a strong signal from Cu_2O but also a significant signal from CuCl as shown in Figure 11. Similarly for shakudo (98Cu2Au, sample S3), a strong Cu_2O 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.

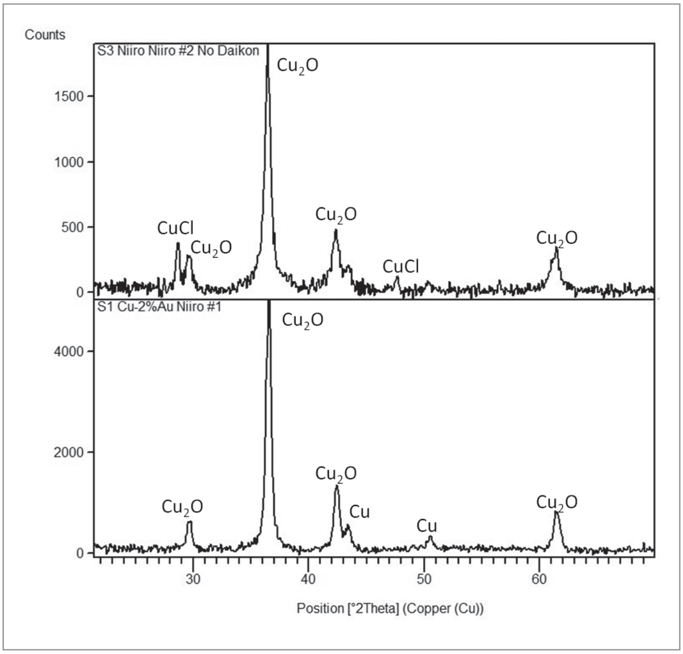

Figure 11 *The glancing angle XRD trace comparing shakudo patinated using Niiro #2 (S3) with Niiro #1 (S1) showing the formation of CuCl in the case of Niiro #2*

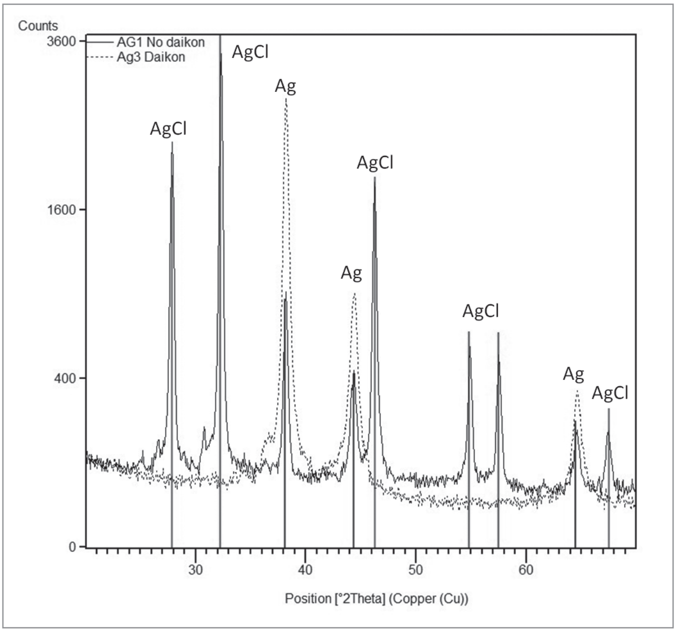

Figure 12 *The glancing angle XRD traces for fine silver patinated in Niiro #2 with (Ag3) and without (Ag1) a daikon pre-treatment showing the formation of AgCl*

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 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.

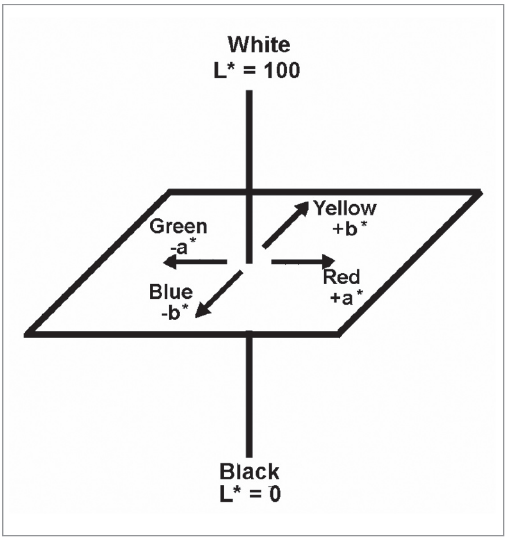

Figure 13 *A schematic of the L*a*b* color space*

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

Pure Copper and Fine Silver

Oxygen-free copper (CW008/C103) was used as a standard to test the effects of varying the niiro parameters. A piece of niiro-colored copper made in Japan in 2001 with a 'good' red appearance was used as a color reference point. Fine silver was also patinated in order to determine the effect of the niiro on silver so that its influence on Ag-Cu alloys could be more easily discerned.

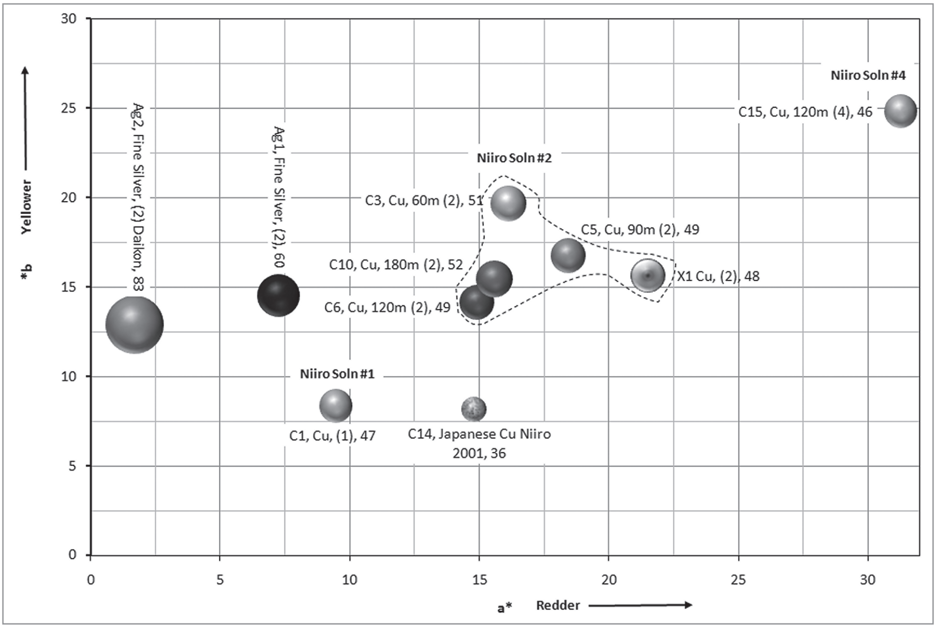

***Figure 14** Graph showing the color of fine silver and copper samples on the a*, b* color map. L* is represented by the diameter of the circle and in the data point label.*

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^*_{daikon} = 83 compared with $L^*_{no\text{-}daikon}$= 60) and b* is reduced by 2 and a* by ~6.

The Japanese copper piece from 2001 (C14) shows a low reflectivity but a dark red color by the naked eye, consistent with its values of L*=36, a*=14.8, b*=8.1. Further study is needed to ascertain the change in color of niiro-colored copper over time. A typical result from Niiro #1 is shown (C1), which has a similar b* value as the Japanese 2001 sample (C14) but is much lower in a* (redness).

The copper alloys patinated using Niiro #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 (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* ~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.

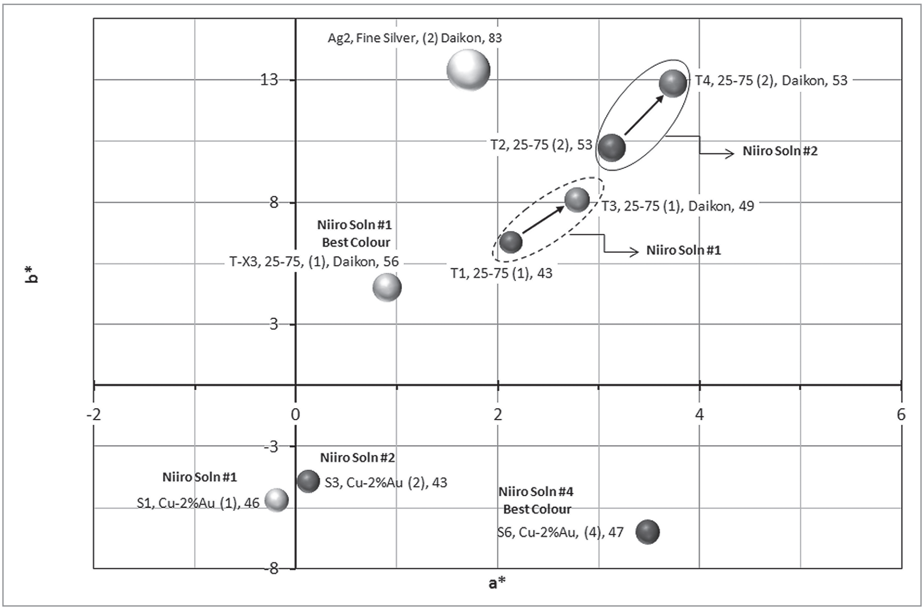

Figure 15 *Graph showing the color of fine silver (Ag2), shakudo (S1, S3, S6) and shibuichi 25-75 (T1-T4 and T-X3) samples on the a*, b* color map. L* is represented by the diameter of the circle and in the data point label.*

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.

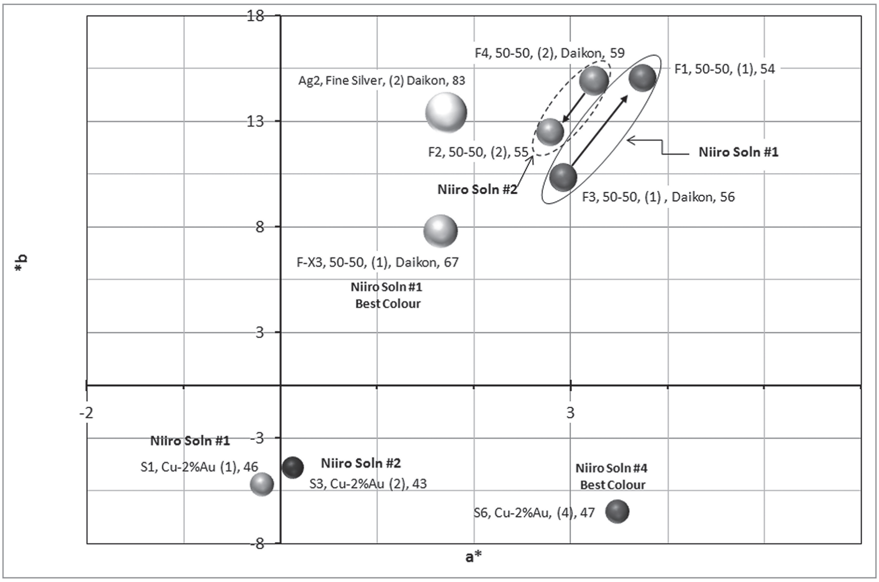

Figure 16 *Graph showing the color of fine silver (Ag2), shakudo (S1, S3, S6) and shibuichi 50-50 (F1-F4, F-X3) samples on the a*, b* color map. L* is represented by the diameter of the circle and in the data point label.*

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.

On 25-75 shibuichi alloys immersed in Niiro #2, the chloride again resulted in higher a* and b* compared with Niiro #1. For 50-50 shibuichi the results for Niiro #1 and Niiro #2 were very close and thus no conclusions can be drawn on the shift caused by the chloride. At the time of writing, shibuichi alloys have not yet been tested using Niiro #3, #4, #5 and #6.

Niiro #4 was a solution made up from laboratory-grade chemicals and contained copper acetate, copper sulfate and sodium chloride but omitted calcium carbonate and plum vinegar. Using this solution on copper and shakudo resulted in some of the best colors produced so far, as shown for copper C15 and shakudo S6. XRD indicated that no chlorides were formed on these surfaces.

Discussion

Casting and Microstructure

A comparison between two traditional workshop casting techniques, steel mold casting and water bath casting, and more modern and controlled continuous casting has been carried out. Three alloys were successfully cast by all three techniques, i.e., shakudo (98Cu2Au), shibuichi 25-75 (Ag-Cu) and shibuichi 50-50 (Ag-Cu).

Comparison of the cast quality, porosity, microstructure and mechanical properties revealed that the continuous casting technique produced consistent and high quality materials with virtually no porosity or other defects but with microstructures and mechanical properties comparable to the workshop-based materials. Water-cast shakudo was particularly prone to porosity and these pores were not always eliminated by rolling, thus increasing the risk of blistering during subsequent use.

Surface segregation of the eutectic phase was observed in the shibuichi continuous cast materials, and care needs to be taken to remove these layers before proceeding with any surface patination techniques, as the microstructure in these layers is quite different from the bulk. Removal before rolling is preferable as the layers persist during rolling and then presents a thinner layer but spread over a much larger surface area, making the task of polishing it off more difficult.

The microstructures of the alloys were different in terms of the amount and distribution of the eutectic phase in the shibuichi alloys and the grain size and gold distribution on the shakudo alloys. These differences were primarily a result of the different cooling rates of the casting techniques. The water casting technique would appear to have the slowest cooling rate. Rolling significantly deforms the microstructure where, for example, a 20µm Cu-rich grain will be spread out to cover more than 100µm. This makes any microstructural textures or inhomogenieties more likely to be visible to the naked eye. The very large crystal size of the continuous cast metal was visible in the surface patina of bowls forged in the studio.

The alloys produced via the different methods had very similar hardness with as-cast shakudo HV55/10, as-cast 50-50 shibuichi HV96/10 and as-cast 25-75 shibuchi HV70/10. On rolling, the work hardening effect increased the hardness to 130, 185 and 170, respectively. Annealing at 550°C (1022ºF) for 30 minutes in a reducing atmosphere was sufficient to fully anneal all the alloys.

Polishing

The effect of traditional polishing materials on the surface texture of copper has been studied. The materials have been ranked in terms of achievable surface texture as shown in Table 4. The best finish achieved was for tsunoko used on already polished copper surfaces where S_a = 12nm. However, since it is a fine abrasive with low material removal rates, it can have difficulty removing the damage created by prior polishes and thus, when used as a part of a sequence, it could only achieve S_a = 65nm.

Silicon carbide powder (1200 grit) appeared to be an effective final polish when used in a sequence with S_a = 48nm. However, variations in the finish achieved using SiC were noted, and this has been attributed to the tendency for the very hard and angular SiC particles to embed in the softer materials. Variations in the level of embedding can come about through the variations in the manual polishing techniques. The use of alternative materials such as alumina (Al_2O_3) and silica (SiO_2), which are less hard and available with different particle sizes and morphologies, needs to be investigated to overcome this problem.

Rokusho and Niiro Compositions

Japanese rokusho has been analyzed and found to consist primarily of copper acetate, sodium chloride and calcium carbonate. The presence of relatively high levels of Zn, Pb, and Sn suggest that it has been produced by the corrosion of brasses or bronzes using acetic acid. The presence of Pb (and other heavy metals such as As) could be a barrier to the more wide-spread use of niiro patination in the West. Using the above results, a suggested composition to be used for the production of a niiro solution based on laboratory-grade chemicals is:

2.65g copper acetate ($Cu(CH_3OO)_2.H_2O$),
0.65g NaCl,
1.7g $CaCO_3$
(the above representing the composition of rokusho)
5g $CuSO_4$ in 1l H_2O
5ml plum vinegar

In order to test the effects of the presence of NaCl, $CaCO_3$, and plum vinegar, four solutions were made up which omitted one or more of these ingredients, and the effect on color and surface composition was tested.

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 (Cu_2O + CuCl/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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