Mater. Res. Soc. Symp. Proc. Vol. 1047 © 2008 Materials Research Society 1047-Y02-01

The Reduction Welding Technique Used in Pre-Columbian Times: Evidences from a Silver Ring from Incallajta, Bolivia, Studied by Microscopy, SEM-EDX and PIXE

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ABSTRACT

A pre-Columbian silver ring from Incallajta, Bolivia, recovered from an archaeological excavation is composed of a thin sheet of silver bent to form the ring. Two small wires in the shape of the infinity sign are joined to the surface of the ring. Four green stone beads were laid inside the four cavities formed by the wires. Energy dispersive spectroscopy (EDX) and Particle Induced X-rays Emission (PIXE) analyses of the beads proved that they were turquoise. Examination with a stereoscopic binocular microscope indicated that the two wires could have been soldered to the ring by reduction welding, because copper corrosion products were found in the interface of the welding, similar to those seen on two modern silver objects from Indonesia, decorated with granulation. Since reduction welding is a technique not reported before in pre-Columbian metallurgy, further analyses were carried out to prove that it was used here. Thus, the ring was analyzed with Scanning Electron Microscopy (SEM-EDX) and external beam PIXE, showing with certainty that the copper content in the area of the welding was higher than in any other part of the ring, with increasing copper amounts towards the center of the weld.

INTRODUCTION

The Incallajta Archaeological Ruins, an archaeological complex of about 30 hectares, in the Municipality of Tocoma, Province of Carrasco, Department of Cochabamba, Bolivia, were appointed a National Monument in 1929 (Figure 1). "The Incallajta Archaeological Research Project" [1] started in 1999 with an extensive systematic survey of valleys, highlands and surroundings undertaken since 2000. Several sites of different epochs were found with agricultural terraces, barns, access control points, water supplies and roads, among other structures. This development shows the great importance of the area for the Incas, whose main occupation dates from 1450 to 1532 A.. D. In 2006 the archaeological excavations in the inner and outer part of structure 52D, toward the west of the site, produced two metallic objects in a carefully protected context around a home furnace and garbage place, indicative that the site was the dwelling of a very important personage. The silver ring is composed of a thin sheet of silver bent to form the ring. Two small wires in the shape of the infinity sign or a figure eight, are joined to the surface of the ring. Four green stone beads were laid inside the four cavities formed by the wires. Figure 2 shows the ring pieces; only one wire was still attached to the ring. The second item is a common sewing needle.

In spite of research done on pre-Columbian metallurgy, still several issues have to be solved. In the spring of 2007, the two small metal artifacts, arrived at the Laboratory of Archaeological Chemistry of the *Instituto de Investigaciones Antropológicas-UNAM* for a technical examination. There were two questions to solve: First, identify the materials composition and its condition to recommend a conservation treatment, and second, determine their manufacturing techniques. The objects came from a site where the neighboring communities were protective of their heritage and extreme care needed to be taken to avoid even minimal damage to the artifacts, so analysis had to be non-destructive. Thus, microscopic examination and analytical techniques such as Scanning Electron Microscopy (SEM-EDX) and external beam Particle Induced X-ray Emission spectrometry (PIXE) were used for the characterization of the artifacts.

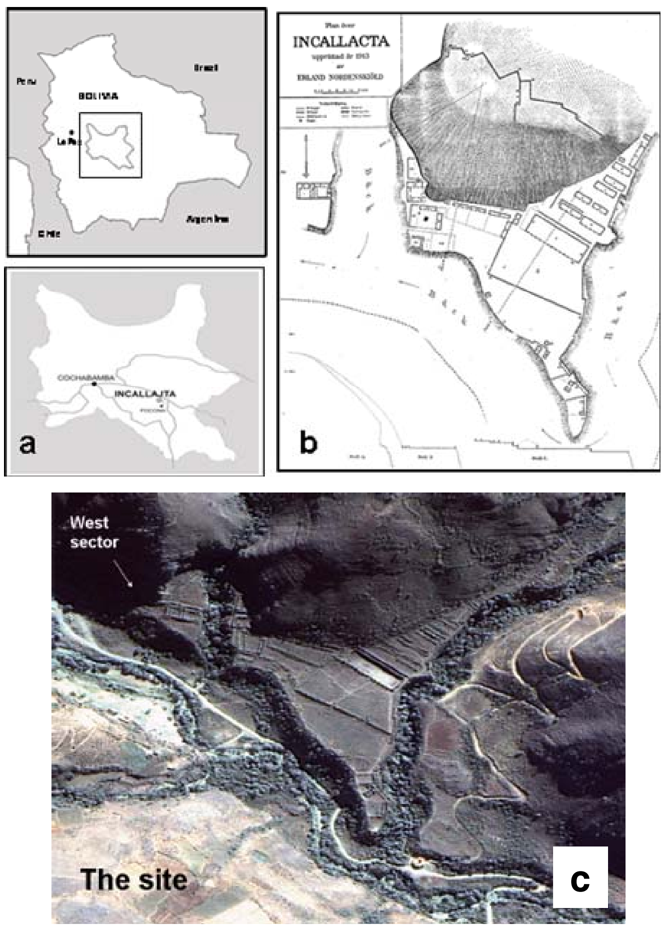

Figure 1. (a) Map of Bolivia showing Cochabamba, (b) historic map of Incallajta and (c) aerial view of the site.

Figure 2. (a) Needle and ring from Incallajta, (b) ring with incrusted green beads.

EXPERIMENT

The microscopic examination of the artifacts was carried out with a binocular stereoscopic microscope at 5 to 50 X to determine the main aspects of manufacturing. After this initial analysis, the other analytical techniques were applied.

Among the analytical techniques that use particle accelerators, Particle Induced X-ray Emission (PIXE), is a very useful tool for analyzing historic artifacts [2] and several non-destructive procedures exist that can be applied to characterize practically every type of material. The object is irradiated with a beam of protons using an external device [3], applied in this case for the analysis of the ring, the beads and needle. All the 3 MeV proton beam irradiations were performed under the observation of a micro-camera that transmits the image of the irradiation zone of the artifacts to two monitors (Figure 3).

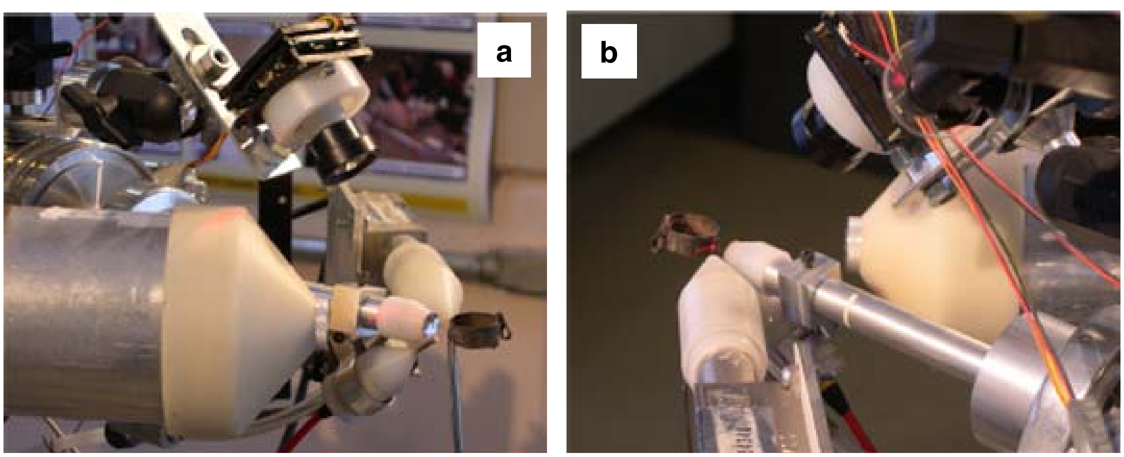

Figure 3. Analysis of the items by the external beam setup. (a) Overview of the instrument and (b) close-up of the beam on the sample.

The beam diameter was collimated to 0.5 mm. Two X-ray detectors were used in the external beam PIXE set-up: an AmpTek Si-PIN diode detector for the detection of light elements and a Canberra LEGe detector for trace element detection. In order to calibrate the external beam for quantitative analysis, standard reference materials certified by NIST of brass (SRM 1107) and homogeneous silver alloys of 0.925 and 0.720 were irradiated under the same conditions as the ring and needle**.** Reference materials of sediments SRM 2704 and 27011 were used as well for the analysis of the green beads.

After the PIXE analysis, the artifacts were studied in the low vacuum electron microscope of the *Instituto Nacional de Investigaciones Nucleares*. Due to their size, they fit inside the SEM chamber without physical harm. Micrographs and EDX spectra were taken using a 20 keV electron beam in regions, where under the binocular microscope, copper corrosion products were evident and also in zones that will enable determination of the original composition of the ring.

RESULTS AND DISCUSSION

Microscopic examination

The examination indicates the technique with which the items were formed: a simple hammering process. The needle was cold hammered from a wire with a technique described by Di Peso and others [4]. The ring was also partially made by cold mechanical work, a thin sheet some 0.2 mm thick and 5 mm wide, curved to form the ring of about 20 mm in diameter. At one end, two nails extended toward the sides and were bent around the other side to hold it firmly. Two small wires bent to form the infinity signs, were applied to the surface of the ring and four green-blue beads were attached in the four hollows they created. It was not clear whether the wires were joined to the ring by mechanical work or if they were welded on. One clue was seen under the microscope: at the interface of the wires and the substrate, and only in this place, a green copper corrosion product was observed (Figure 4), with properties similar to those described for malachite by Gettens [5]. Malachite is a basic copper carbonate, a common copper alteration product. The explanation for the presence of malachite in that place is that the solder was richer in copper, which corrodes preferentially because is more active than silver.

Figure 4. Wire over the ring with green copper corrosion products (inside the indicated region).

Similar localized copper corrosion was observed during microscopic examination of two modern Indonesian silver artifacts, a wrap for cigarette lighters and a container for matches, decorated with "granulations" similar to the ones in ancient gold jewelry, joined to the metal substrate (Figure 5).

Figure 5. Indonesian silver wrap with granulations and detail.

This localized corrosion resulting in malachite was observed in the joins of the attached wires to the body of the ring. The granulation technique was used in gold artifacts, not in silver, by Egyptians, Etruscans and later other countries of Europe until the Middle Ages [6]. Jewelry of gold was decorated with small gold spheres, up to $900/cm^2$, welded to the surface of the metallic artifact. However, the granulation technique was forgotten and when goldsmiths attempted to reproduce it, heat applied to the spheres to weld them to the substrate metal formed a layer of gold on the surface because the spheres fused before the solder. In the 20th century forgeries were produced. Litteldale rediscovered in the 1940's the technique of fusion welding at the British Museum. The weld is obtained when a mixture of an organic adhesive and a copper salt is used to glue the spheres to the object. When this mixture is heated with a blowpipe, the organic adhesive burns providing C and the copper salt is reduced, depositing pure copper that diffuses and welds the spheres to the artifact, without melting them. Thus if malachite is used as copper salt $Cu_2CO_3(OH)_2$, it is reduced to metallic copper when heat is applied, taking the oxygen from the salt according to the reaction of equation 1, the copper then serves as solder:

$$CuCO_3(OH)_2 + C \rightarrow 2Cu + 2CO_2 + H_2O \qquad (1)$$

To find out if Cu was present and if its concentration is higher in places where the welding took place, without removing a sample, SEM-EDX and PIXE analytical techniques were used.

SEM-EDX analysis

Figure 6, shows some micrographs from a turquoise piece and the separated wire. The elemental composition of the ring is shown in Table I. From the EDX results it is clear that the electron beam does not penetrate deeply under the surface of the ring, since the elemental chemical composition is mainly representative of a layer with a certain amount of corrosion, however is possible to find differences between the composition at the join and that of the silver ring that can be interpreted as larger amount of copper and its corrosion products in the joins as related to the surface of the ring and wires. However, in some parts of the wire-ring interface, the evidence is confused by the presence of soil from Si, Al and O contents as well as other elements from the corrosion layers such as sulphur.

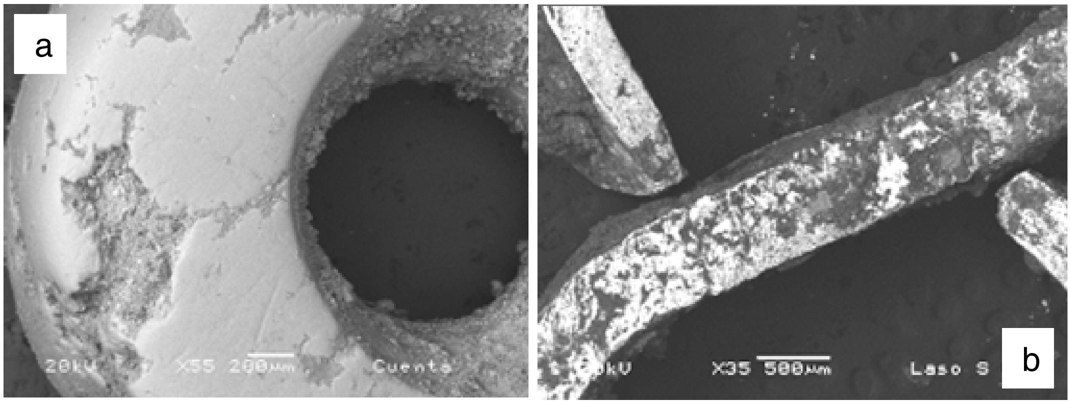

Figure 6. SEM images of the (a) turquoise piece and (b) the separated wire of the ring.

Table I. Elemental composition (weight %) of the ring obtained by EDX.

	Region				
	ring	**welded joint**	**welded joint**	**attached wire**	**separated wire**
C	16.8	23.6	28.0	13.5	13.5
O	24.9	29.6	31.3	24.4	9.33
Na	1.11	0.96	1.10	0.55	0.53
Mg	0.32	0.34	0.38	0.54	0.14
Al	2.82	3.85	4.66	7.99	1.66
Si	4.10	5.45	6.45	4.75	1.33
P	0.62	1.06	1.57	0.78	3.56
S	2.05	0.73	0.51	2.20	0.31
Cl	0.63	0.87	1.16	0.72	0.60
Ca	0.94	1.02	1.63	1.17	0.52
Fe	1.01	1.80	2.70	1.85	68.5
Cu	0.78	1.71	1.69	1.35	-
Ag	43.9	29.0	18.9	40.2	-

On the other hand, the needle presented the following elemental composition: C 29.8 %, O 29.4 %, Mg 0.29 %, Al 3.46 %, Si 5.61%, P 1.5 %, S 0.18 %, Cl 0.48 %, Fe 1.37 %, Cu 24.1 % and Sn 12.9 % indicating that it was a bronze needle but very corroded. It is also contaminated with materials from the soil, indicated by high amounts of O, Si, and Fe.

In regard with the green bead analyzed by this technique, it presents a high proportion of C: 11.6 %, O 48.6 %, Al 16.2 % P 13.0%, Fe 5.4 % and Cu 4.65 %. From the contents of Al, P and Cu contents we can identify the green stones as turquoise.

External PIXE analysis

The elemental composition of the ring determined by PIXE is shown in Table II. The composition of the ring shows an average of Ag 84.9 %, Cu 7.4 % and O 7.4%. The ratio of Cu/Ag for several parts of the ring (A, B, C) and the wire rings indicates that they were made of the same alloy. The variable proportions of Fe and O are due to soil remains, however, the surface corrosion does not seem to have significantly influenced the analytical results due to the depth penetration of the 3 MeV proton beam (about 30 μm for this metallic matrix) [7].

Table II. Elemental concentrations (weight %) of the ring determined by PIXE. Uncertainties are ±10% of the measurement.

Analyzed Region	Fe %	Cu %	Ag %	O %	Cu/Ag ratio
wire 1_1	0.08	10.0	85.4	4.5	0.12
wire 1_2	0.08	6.6	89.9	3.4	0.07
wire 1_3	0.08	4.9	89.8	5.2	0.05
wire ring 1_4	0.17	8.0	83.7	8.1	0.10
ring A	0.07	9.4	84.0	6.4	0.11
ring B	0.06	7.2	88.9	3.9	0.08
ring C	0.38	6.7	82.0	10.9	0.08
wire ring 2_1	0.28	8.4	82.9	8.4	0.10
wire ring 2_2	1.78	5.4	77.1	15.7	0.07
welded joint ext.	2.49	51.8	36.9	8.9	1.4
welded joint med.	0.32	69.4	11.9	18.4	5.8
welded joint center	0.37	70.4	12.7	16.5	5.5

In the region where the weld may be present, and as the PIXE analysis goes deeper than EDX into the inner part of the core, the concentrations of Cu increase rapidly from the exterior (51.8%) to the center of this region (70.4%), reinforcing the possibility that a reduction welding method could have been used to join the wires to the rings [6]. Soldering cannot have been used if we consider that an alloy composition of 70%Cu-30%Ag will fuse at 950°C, about 70°C higher than the fusing temperature of the silver ring alloy with a composition of 90%Ag-10%Cu [8]. This is the first report of this kind of soldering technique for pre-Columbian America.

On the other hand, the mean analytical results from PIXE for the needle agree with the EDX results and indicate that its alloy is a Cu-Sn bronze, (Fe 0.18%, Cu 50.1%, As 0.04%, Sn 31.9%, Sb 0.17%, O 17.6%). It is not possible to measure the composition accurately due to the advanced degree of corrosion and the needle is so thin that the composition of the whole metal core has been altered. The high amounts of Sn and Sb are due to surface enrichment in the patina layer.

Table III shows the elemental composition of the green beads. Due to the observed proportions of Al, Cu. and P, the beads mineral identification corresponds to turquoise. The Fe and Zn seen in the analysis is due to substitutions of Cu and Al in the turquoise crystalline structure, which could correspond to other phases such as calcosiderite and faustite [9]. The comparison of the compositions of the beads indicates that they were obtained from different sources, with the compositions of beads 1 and 2 the most similar.

Table III. Elemental concentrations (weight %) of the green beads determined by PIXE. Uncertainties are ±10% of the measurement.

Item/region	**O**	**Al**	**P**	**Cl**	**K**	**Ca**	**Ti**	**Fe**	**Cu**	**Zn**
	%	%	%	%	%	%	%	%	%	%
bead 1_1	45.6	20.0	21.0	0.046	0.069	0.083	0.013	3.63	7.34	2.21
bead 1_2	44.9	20.0	20.0	0.099	0.120	0.109	0.008	3.50	8.98	2.29
bead 2_1	37.3	26.4	27.1	0.027	0.191	0.100	0.041	1.41	6.77	0.81
bead 2_2	41.5	25.2	24.9	0.096	0.184	0.117	0.021	1.26	6.00	0.77
bead 3	46.3	20.6	18.0	0.097	0.185	0.086	0.078	1.54	12.45	0.64
bead 4	47.6	17.5	20.7	0.039	0.046	0.044	0.020	6.04	7.67	0.38

CONCLUSIONS

The microscopic examinations and the analytical results of the copper elemental concentration profile indicate that reduction welding has been used to join the wires to the silver ring discovered in Incallajta. The use of this technique has never been reported before in pre-Columbian metallurgy.

Besides the corroded surface, PIXE analysis was useful in characterizing the silver ring and the wire rings alloys and in determining the copper content of the weld due to the higher penetration of the proton beam. Unfortunately, the corrosion layer was too thick to obtain representative measurements using SEM-EDX.

The needle was manufactured using a Cu-Sn bronze. Finally, green stone beads were identified as turquoise from EDX and PIXE results. This is the first report of the use of this mineral in this region of pre-Columbian Bolivia. The compositional data of the green beads will be useful for turquoise sourcing in the future.

ACKNOWLEDGMENTS

Authors would like to thank technicians K. López and F. Jaimes for their support at the Pelletron particle accelerator during PIXE measurements. Partial financial support was provided by CONACyT Mexico grant U49839-R.

REFERENCES

1. M.A. Muñoz Collazo, 2006. Gestión Participativa del Patrimonio: Un caso Boliviano, *Cuadernos de Antropología y Patrimonio Cultural* 4. INAH-CONACULTA, Mexico, 3- 47.
2. M. A. Respaldiza & J. Gómez-Camacho (eds.), 1997. *Applications of Ion Beam Analysis Techniques to Arts and Archaeometry*, Universidad de Sevilla, Sevilla.
3. J.L. Ruvalcaba Sil. 2005. Analysis of Pre-Hispanic Items from Ancient America in *X-rays in Archaeology*, M. Uda, G. Demortier, I. Nakai, coord, Springer, Dordrecht,123-149.
4. Ch.C. Di Peso, J. B. Rinaldo and G. J. Fenner, 1974. *Casas Grandes. A Fallen Trading Center of the Gran Chichimeca*. Vol. 7 Stone and Metals. The Amerind Foundation Inc., Northland Press, 500-532.
5. R.J. Gettens, 1963. *Mineral Alteration Products in Ancient Metal Objects* in Recent Advances in Conservation, G. Thomson, Editor, Butterworths, London, 89-92.
6. G. Nestler, E. Formigli, 2004. *Granulazione Etrusca, Un'antica tecnica orafa*, Nuova Immagine Ed., Siena.
7. L. Beck, S. Bosonnet, S. Réveillon, D. Eliot, F. Pilon, 2004. Nuclear Instruments and Methods B 226, 153-162.
8. T.B. Massalsi, 1992. *Binary alloy phase diagrams*, ASM International, Ohio, 29.
9. J.L. Ruvalcaba Sil, L. Bucio, M.E. Marín & A. Velázquez, 2005. Estudio por XRD y haces de iones de teselas de un disco de turquesas del Templo Mayor de Tenochtitlán in *La Ciencia de Materiales y su Impacto en la Arqueología. Vol II*, Academia Mexicana de Ciencia de Materiales A.C., D. Mendoza, J. Arenas y V. Rodríguez coord., Ed. Lagares, México, 95-11.