THE PATINA OF CHINESE BRONZES WITH A HIGH TIN CONTENT

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Whenever the tin content of a bronze is higher than 15 %, we note the appearance of an "δ" intermetallic phase with a high content tin, hard, brittle, of a silver white colour. It looks like a typical "eutectoid " microstructure, closely associated with a copper-rich and yellow-coloured "α" phase.
All bronzes whose tin content is higher than 20 %, and whose δ phase is very high thus display a silvery colour, and because of their harness, allow doing a very thorough polishing work. (1).

Bronze craftsmen have been using this method for the purpose of melting mirrors, whose brightness allowed " lighting the world beyond " (2).
They also used these alloys for manufacturing jars and ritual objects, which, at the time, must have been looking like pale silver.

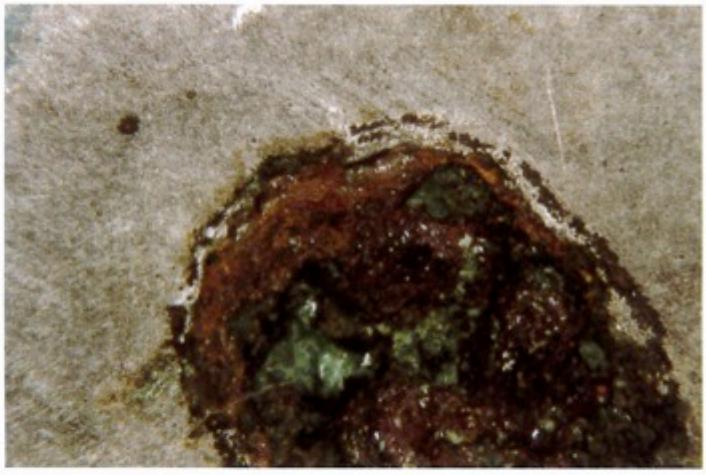
Although some of these objects may appear not to have lost their gloss or their colour over the centuries (a description of the patinas of mirrors was made as far back as the Song Shui - Yin-Qin dynasty: " quick-silver white" (3) many of those have developed into magnificent patinas with a greenish-grey shade, sometimes called "water patina" (4) (Qian-Bei: " lead grey ", Lu-Qi-Gu: " green lacquer antique "), blue or black-coloured (Hei-Qi-Gu; " black lacquer antique").

These patinas, often compared to lacquer, are outstanding, since the original surface of the object appears to be intact, with all the engraving motifs and bronze work, as well as the shiny or satin-like gloss of metal.
They are, however, very fragile and display occasional superficial flakes showing a more or less thick blue or green-coloured layer above an oxidised metal.

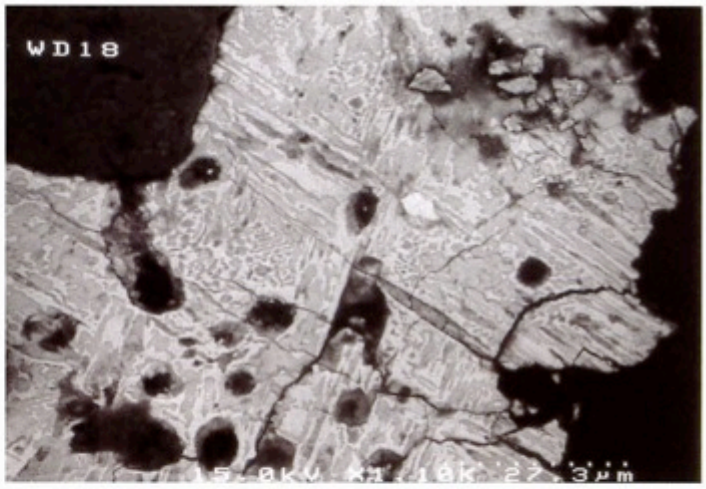
These objects also display " eruptions" of coloured products caused by a more pronounced oxidation of copper or lead, which entails the splitting of the patina layer and covers it with incrustations.

■ **Any object, whose surface is silver-coloured**, as is the case with mirrors, is one who best allows observing the original condition of bronzes.
Preferably, the superficial oxidation has eliminated the alloy's α phase and the lead addition, which was meant to make easier the metal casting, whose only remains are circular marks of globules.

On the object's surface the acicular δ intermetallic phase remains intact, and displays a jagged graphic design, whose abundance gives the object a silvery colour.



Bronze mirror (stereomicroscope, x20)
The polished silver-like surface of this bronze mirror is locally destroyed by an in depth development of copper elements (oxides and carbonates).

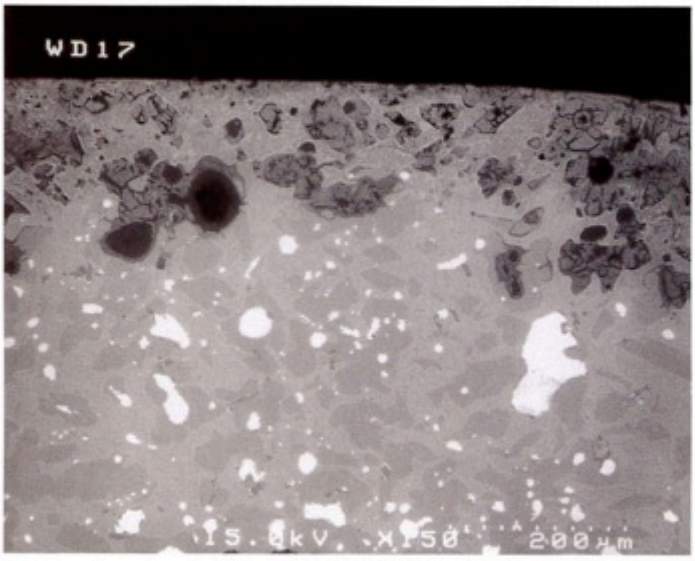


Bronze mirrors (SEM, BSE, x 1100)
The cracked surface of the bronze mirror displays a continuous, silver - coloured δ intermetallic phase, with an acicular morphology. Dark, or more or less circular shapes, point to the presence of the alloy's lead globules, which were eliminated by corrosion.

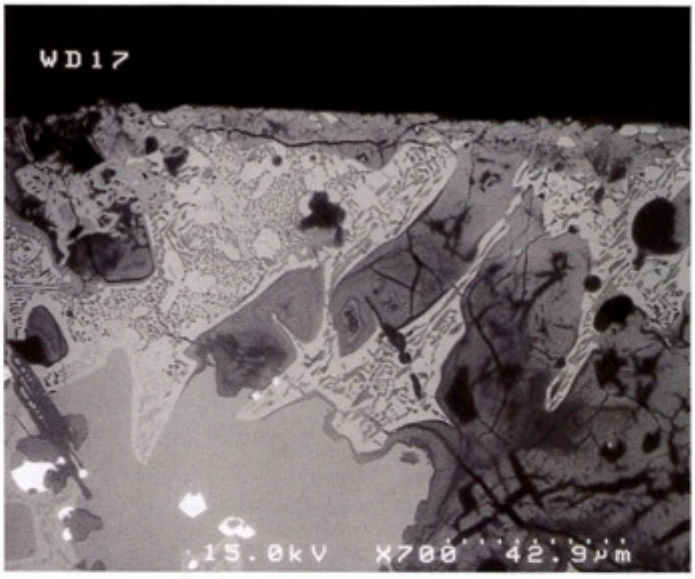
■ **Greenish-grey "water patinas"** correspond to a different and more pronounced corrosion type.

With respect to these objects, the δ phase remains intact, whilst the copper and lead of the a phase are preferably erased from the metal's surface. The tin's corrosion elements - mostly consisting of tin oxides - are insoluble and remain "in situ". Thus, a pale grey tin-enriched layer slowly develops, and is more or less coloured by copper and lead salt remnants.

Lid of a KUANG jar (stereomicroscope, x75)
The patina has kept almost intact the slightly glossy surface of this bronze, whose incisions were originally underlined by the encrustation of a crushed quartz-based white element..



Metal section from the lid of the KUANG jar (SEM, BSE, and x150).
Underneath the metal's original surface, we note the gradual replacement of the a phase by tin oxides, as well as the preferential dissolution of lead globules, the only remnant of which is a dark circular mark.

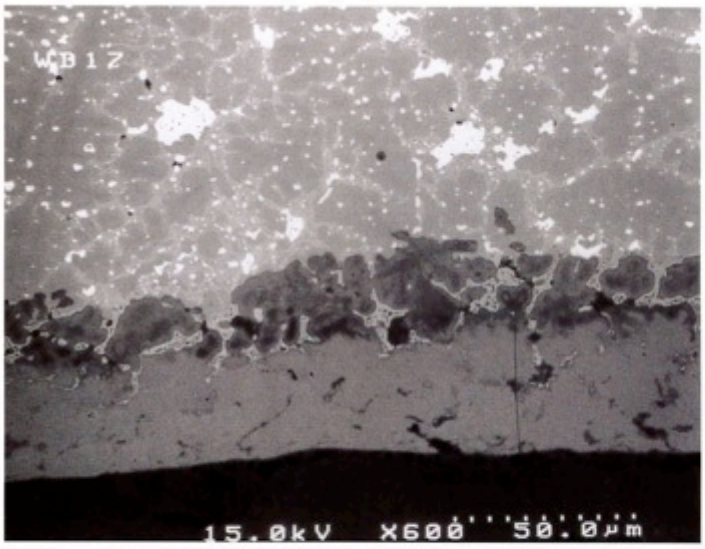


Metal section from the lid of a KUANG jar (SEM, BSE, and x700)
In the tin-enriched layer, the α acicular intermetallic phase (light-coloured in the enclosed picture) remains intact, whereas the α phase has been altered (dark grey phase shown in the enclosed picture). Rounded circulars shapes correspond to the location of lead globules.

■ Under certain ground burial circumstances, more advanced corrosion processes shall also cause the disappearance of the δ phase, whose acicular structure can still be observed in the shape of "ghosts" in a completely **mineralised layer** consisting of a mixture of tin oxides, scattered lead and chemical elements, such as silicon, iron, aluminium, potassium, phosphorus, etc...resulting from the object's environment.

Such a mineralization causes the development on the object's surface of slightly translucent blue, green, yellow or green-coloured layers. This very phenomenon is the one that created magnificent black patinas, especially spectacular in the case of bronze mirrors (5).

Lid of a YU jar (stereomicroscope, x15)
The metal section shows a very coloured and translucent mineralised layer,with a varying thickness. A fine oxidised metal layer keeps it separate from the unaltered sound metal (black-coloured in the picture).



Lid of a YU jar (SEM, BSE, x600)
Observing the object under the scanning electronic microscope (SEM) reveals the presence of "ghosts" from the δ intermetallic phase in the mineralised layer (medium grey layer, bottom of the picture). The δ phase is seen to be intact in the intermediate oxidised layer with the "sound" metal (top part of the picture).

(1) : N. MEEKS, 1993 – Surface characterization of tinned bronze, high tin bronze, tinned iron and arsenical bronze. Metal plating and Patination, Butterworth-Heinemann, Oxford.

(2) : W.F. COLLINS, 1934 – The mirror-black and " quick-silver " patinas of certain Chinese bronzes. Journal of the Royal Anthropological Institute, LXIV.

(3): RJ GETTENS, 1969 – The Freer Chinese Bronzes, Vol. II, Technical Studies. Smithsonian Institution, Freer Gallery of Art, Oriental Studies, N°7, Washington.

(4) ZHU SHOUKANGand HE TANGKUN, 1993 – Studies of ancient Chines mirrors and other bronze artifacts. Metal plating and Patination, Butterworth-Heinemann, Oxford.

(5) N. MEEKS, 1993 – Patination phenomena on Roman and Chinese high tin bronze mirrors and other artifacts. Metal plating and Patination, Butterworth-Heinemann, Oxford