Applications of Electron Backscatter Diffraction (EBSD) in Archaeometry

Introduction

Archaeometry is the application of scientific techniques developed for the physical and biological sciences to archaeology. EBSD has become relatively common in materials science characterization laboratories all around the world, however, its application to archaeological studies is still relatively new.

This application note shows three different examples of the use of EBSD in archaeological applications. The first example demonstrates the use of EBSD to characterize the raw materials and phases originating during the manufacture of colored glassy mosaic materials. The second is the analysis of crystallographic texture and carbide precipitation in wootz steel sword blades to infer their thermo-mechanical history. The third example shows how EBSD has been used to study the embrittlement of an ancient silver cauldron.

Mosaic Material

Mosaic patterns are formed from small pieces of stone or glass called tesserae. Figure 1 shows a sample of red opaque glassy material from which tesserae were prepared. This sample is part of a large set found in Siena Cathedral in Tuscany, Italy and comes from the 13th-14th century. The old Tuscan recipe books do not include any information on these types of glasses. Thus, materials characterization techniques have been applied to determine the technique, origin and period of production.

Opaque red glass is usually characterized by small metallic copper or cuprite particles (<10 μm) embedded in the microstructure. However, the microstructure observed in these samples was more characteristic of transparent glasses. In this sample, both nanometer and micrometer sized particles bearing copper were observed. The larger particles sometimes contained lead spots. Wavelength Dispersive Spectrometry (WDS) analysis of these particles (700-800 m) showed some iron bearing heterogeneities.

The "phase ID" process was used to analyze these materials. In this process the chemical species present (typically determined by Energy Dispersive Spectroscopy (EDS) or WDS) are used to compile a list of candidate phases, typically from a large database of known phases. An EBSD pattern is then captured from the area and indexed using the crystallographic structure data for each candidate phase. The indexing results are ranked by how well they match the pattern to identify the most probable candidate phase. In this example, the phase ID process was used to analyze both the copper and iron bearing areas.

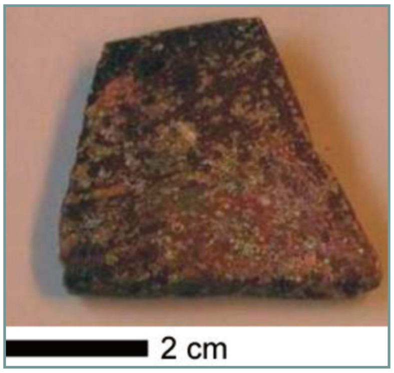

Figure 1. Mosaic material.

The copper bearing areas showed the presence of tin oxide and the absence of other elements such as oxygen and zinc. This would seem to exclude the use of copper oxides and brass as source materials. The chemical species present as determined by WDS were used to compile a list of 20 candidate phases. Ten different EBSD patterns from the copper bearing area were obtained. Figure 2 shows an example of the poor match found for copper oxides and copper-tin compounds (as expected from the chemical analysis) and that the best fit was obtained for metallic copper. However, the crystal structures of metallic copper and low-tin bronze are quite similar and thus difficult to distinguish using EBSD.

These results suggest that bronze was used as a copper source although two other possibilities are plausible as well. The existence of the tin and lead may be due to copper ores lying together with tin and lead ores, which is the case in several Tuscan mines. Another possibility is that different compounds may have been intentionally introduced, such as metallic copper, lead stannate ($PbSnO_3$) or cassiterite (SnO_2). However, these likely would have melted and mostly diffused into the glass except for a rare few solidifying as small droplets.

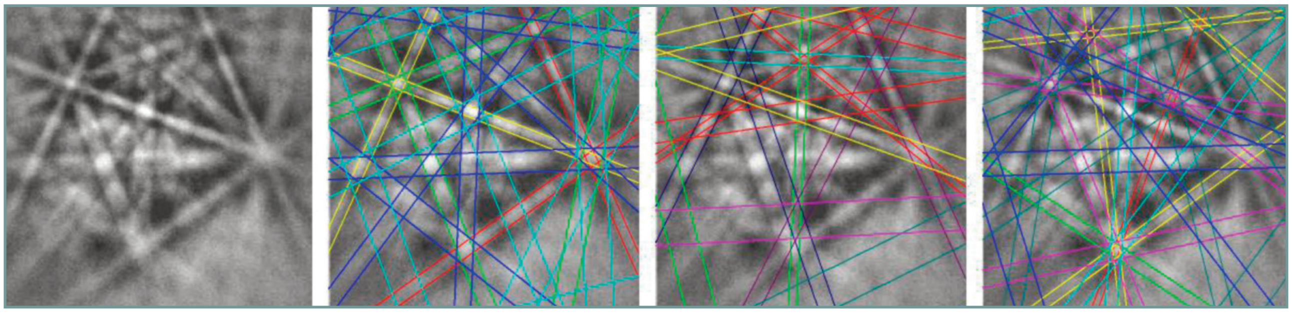

Figure 2. An EBSD pattern from a large copper bearing particle, indexed as copper, a monoclinic copper oxide phase, and a hexagonal copper-tin phase.

The phase ID process was also applied to the iron-bearing heterogeneity assuming the most common crystalline phases of iron oxides, namely wüstite (FeO), hematite (Fe_2O_3) and magnetite (Fe_3O_4) as candidate phases. Magnetite was found to be the most likely phase. This result suggests that iron was introduced into the melted glass as iron-ore (which may contain magnetite) or iron scraps containing partially oxidized grains (present in worked iron materials). The iron introduced in this form created a favorable condition for the formation of the colloidal metallic copper suspension.

Wootz Steel Sword Blades

Wootz steel would now be termed an ultra-high carbon steel (1-2%). It originally came from southern India in the Deccan region. India has a long history of steel making going back as far as Alexander from the third century B.C. Arabs took ingots of wootz steel to Damascus to form the blades famous for their quality and swirled patterns. Blade makers still strive to mimic these beautiful patterns today and thus there has been a continual interest in wootz steel from ancient to modern times. Despite the longstanding interest in wootz steel by blacksmiths and scientists, unanswered questions still remain about the specifics of the techniques used by the ancient blacksmiths to forge implements of wootz steel.

Barnett, Sullivan and Balasubramamaniam (2008) have used the modern technique of EBSD to study an ancient wootz steel sword blade to infer aspects of the process employed in producing the blade. A sample was cut from a wootz still sword shaft and scans were performed at three different locations as shown in Figure 3.

At each point in an EBSD scan a pattern is captured and indexed automatically by the computer. In addition to the crystallographic orientation obtained by indexing the pattern, a metric describing the quality of the pattern is also recorded. Figure 4 shows two gray scale maps constructed using this quality metric. The pattern quality is affected by the material in the interaction volume (cementite vs. ferrite for example), the deformation state of the material (deformed material typically produces more diffuse EBSD patterns than recrystallized material) or other factors such as the presence of grain boundaries. In the maps shown in Figure 4, the shape, size and distribution of the carbides can be observed. From the morphology of the carbide, we can discern something about the forming process used to produce the blade. Scan A (near the cutting edge of the blade) showed a distribution of carbides with a relatively fine distribution relative to the blocky carbide structures observed in scan B (near the trailing edge).

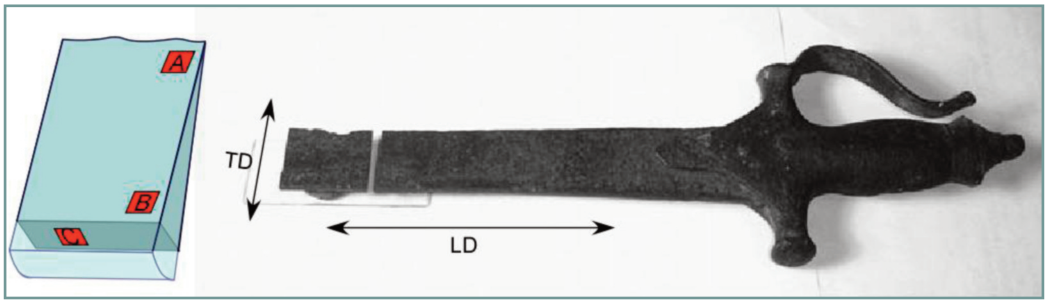

Figure 3. A wootz steel sword and schematic showing the locations of EBSD scans.

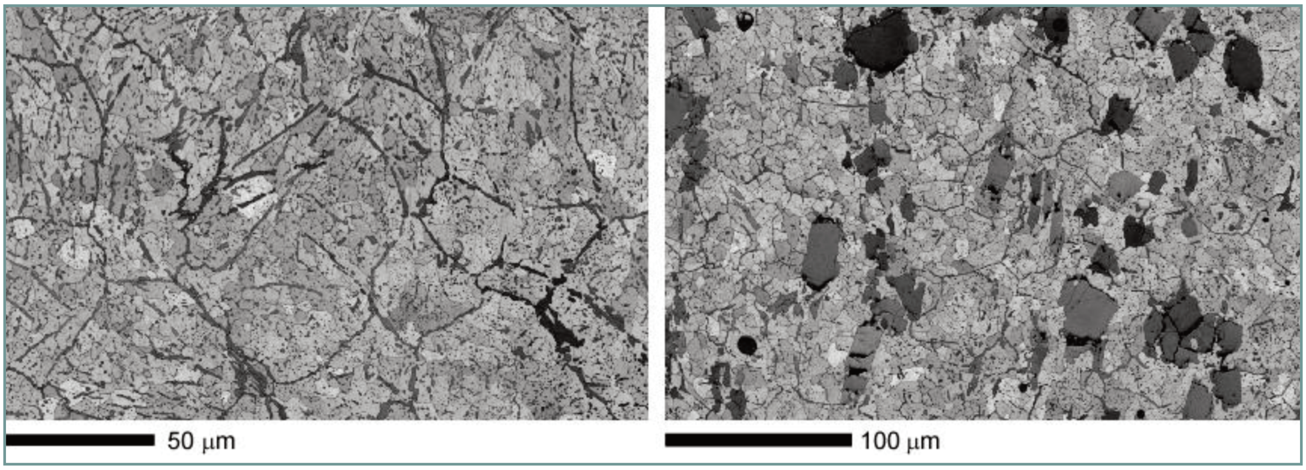

Figure 4. Gray scale maps constructed from pattern quality data for the EBSD scans at locations A (left) and B (right).

Figure 5 shows the crystallographic textures presented as inverse pole figures, as calculated from the orientation data recorded during the EBSD scans. Inverse pole figures show the crystallographic poles aligned with specified sample directions. The ferrite textures are clearly much more random than those from the cementite. There are some subtle differences between the cementite textures at the cutting edge of the blade (scan A) as opposed to the back edge (scan B), the most notable being a stronger alignment of the (010) planes at the cutting edge. However, not too much should be inferred from these differences as they may simply arise from lack of a fully statistically reliable sampling. In fact, it is notable that the textures are so similar between scans A and B given their markedly different microstructures.

The [010] ND texture observed in the carbides accompanied by a random texture in the parent ferrite grains suggests that the hammer blows used to forge the blade were directed normal to the blade surface as would be expected. It was also observed that the coarse carbides were clustered together in regions of similar crystallographic orientation. This suggests that coarse carbides were formed during the original cooling of the wootz cake. The orientation clustering observed, coupled with the texture results, suggests that the hammer blows were directed in the same direction from the initial forging of the blade through the end of the process. This has been confirmed by similar analyses of other wootz steel artifacts.

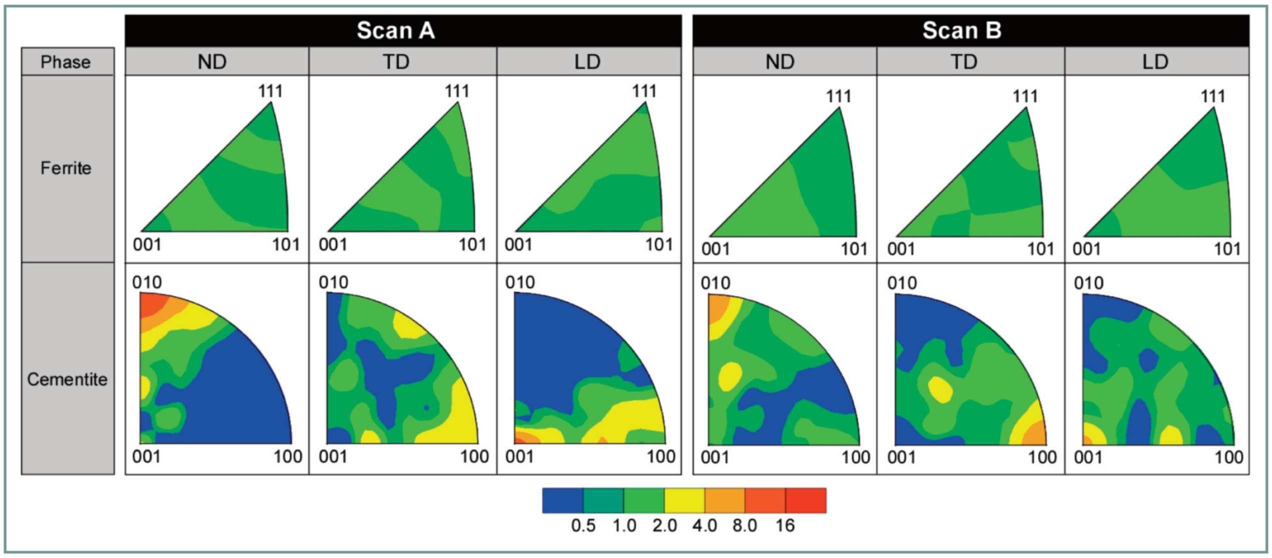

Figure 5. Ferrite and cementite textures from scans A and B plotted as inverse pole figures.

Figure 6. The Gundestrup Cauldron.

Silver Embrittlement

Ancient silver can be embrittled by long-term corrosion and microstructural changes. Understanding silver embrittlement is critical to the restoration and preservation of ancient silver artifacts. There are three basic types of embrittlement, corrosion-induced, microstructurally-induced, and the synergistic combination of the two. The most common form is corrosion-induced since it occurs in mechanically worked and annealed objects, which constitute the majority of artifacts especially in the Old World. It is a consequence of low-temperature discontinuous segregation of copper at grain boundaries and/or slip lines in objects that were not annealed after mechanical forming. Examples include struck coins or decorating by chasing or stamping.

Figure 6 shows a picture of the reassembled Gundestrup Cauldron. The object was found in a peat bog near Gundestrup, Denmark and is now housed at the National Museum in Copenhagen. The cauldron is the largest surviving silverwork from the European Iron Age, dating to the first or second century B.C. It is constructed of twelve plates and a bowl. Its size, quality of workmanship and iconographic variety have made it a popular study subject. Yet, its origin remains controversial largely because the style of workmanship and iconography are inconsistent with each other. The silver content ranges from 95 to 98%. Copper is the main alloying (or impurity) element.

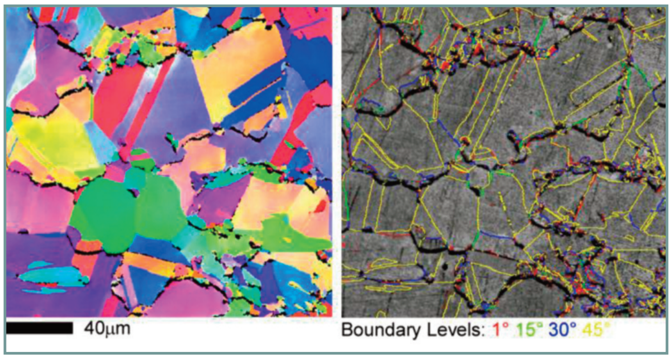

Figure 7. Orientation map and IQ map overlaid with boundaries colored according to misorientation for a sample from the Gundestrup Cauldron.

Wanhill (2007) has used EBSD to investigate the microstructure of four small samples taken from different parts of the cauldron. The EBSD analysis results fall into two categories:

(1) One of the samples (Figure 7) exhibited an annealed microstructure virtually free of corrosion despite extensive evidence for discontinuous precipitation of copper at grain boundaries.

(2) Figure 8 shows the range of microstructures observed in the other three samples. These samples show evidence of corrosion damage and deformation. The deformation manifests itself in the orientation maps as color variations within grains and the density of low angle grain boundaries (i.e. the red boundaries). The black regions are due to cracks, primarily intergranular but some transgranular as well. No evidence for discontinuous precipitation was observed.

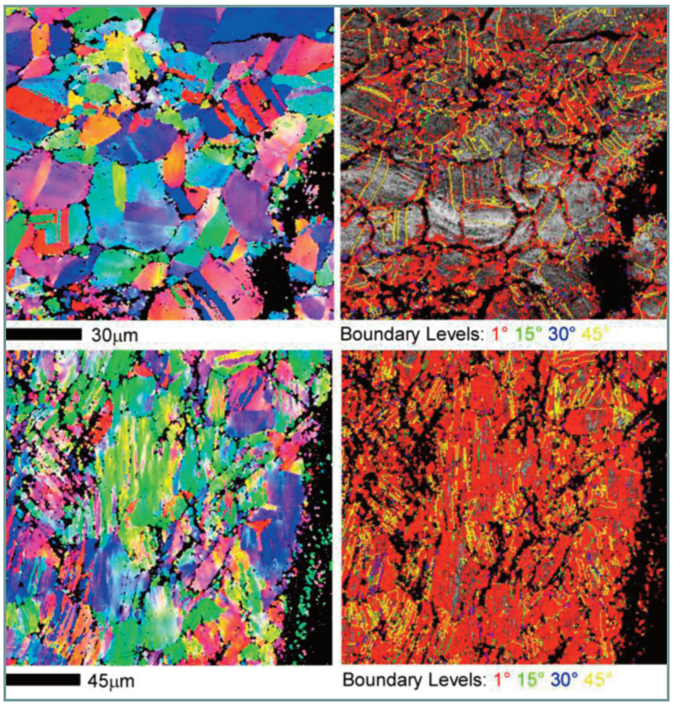

Figure 8. Orientation map and IQ map overlaid with boundaries colored according to misorientation for two samples from the Gundestrup Cauldron.

The differences between these samples show that corrosion was primarily due to cold-deformation as opposed to discontinuous precipitation. These results are consistent with other observations of intergranular corrosion and cracking in ancient silver.

Conclusion

- EBSD can be used in conjunction with EDS and WDS to identify crystalline phases in materials to aid in the identification of the source materials of various artifacts. As these are all Scanning Electron Microscope (SEM) based techniques, this analysis can be done on very small samples such as paint pigments.
- EBSD can also be used to characterize the preferred crystallographic orientation or texture in materials. This can help identify specific processes used in forming an object.
- EBSD can be used to understand the state of a material, i.e. if it is in a cold-worked or heat-treated state. This can be done at the microscopic scale to aid an archaeologist to preserve and/or restore an object of historical significance.

Acknowledgements

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Bibliography

For more details on the examples presented here see:

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M. R. Barnett, A. Sullivan and R. Balasubramaniam (2009). "Electron backscattering diffraction analysis of an ancient wootz steel blade from central India." *Materials Characterization* **60**: 252-260

A. Sullivan and M. Barnett (2010). "EBSD Study of Indian Wootz Steel Artifacts to Infer Thermomechanical History by Observation of Carbide Distribution and Orientation." *Microscopy Today* **18**: 16-25

R.J.H Wanhill (2007) “Embrittlement of ancient silver.” *Journal of Failure Analysis and Prevention* **5**:41-54.

Another publication showing the application of EBSD to archaeological artifacts:

C. Mapelli, W. Nicodemi, R. F. Riva, M. Vedani and E. Gariboldi (2009). "Nails of the Roman Legionary at Inchtuthil." *Metallurgia Italiana* **101**: 51-58

The following publications are cited in the text.

1. S. Srinivasan and S. Ranganathan (2004) “Wootz Steel: An Advanced Material of the Ancient World” http://materials.iisc.ernet.in/~wootz/heritage/WOOTZ.htm