EFFECT OF POROSITY IN THE MICROHARDNESS OF AN ALBANIAN-DALMATIAN AXE (XIII-XII B.C.) AND A CELT ONE (XI-X B.C.) EXCAVATED IN NORTHERN ALBANIA

OLTA ÇAKAJ[1], EDLIRA DUKA[2], TEUTA DILO[1], NIKOLLA CIVICI[3], FREDERIK STAMATI[4]

[1]Faculty of Natural Sciences, University of Tirana, Tirana, Albania

[2]Faculty of Mathematical Engineering and Physical Engineering, Polytechnic University of Tirana, Tirana, Albania

[3]Institute of Applied Nuclear Physics, University of Tirana, Tirana, Albania

[4]Academy of Albanological Studies, Tirana, Albania

e-mail: olta.cakaj@fshn.edu.al

Abstract

At the center of this study is an Albanian-Dalmatian axe (XIII-XII B.C.) and a celt one (XI-X B.C.) excavated in the suburbs of Shkodra. The porosity and the microhardness of these bronze axes (copper-tin alloy) were studied using image analysis and the Vickers microhardness test. All the measurements were performed on a 4mm^2 sample that was permitted to be removed from each axe. Pores in metallic alloys are created mostly during solidification, after casting, because of gas evaporation such as oxygen. The pore surfaces became stress concentration zones which leads to the alloys microhardness decrease. The more ancient is the object the more non sophisticated is the production process, creating microstructures with pores, cracks, etc. The mean porosity resulted to be 8.76 ± 0.09% for the celt axe and 2.06 ± 0.105% for the Albanian-Dalmatian one (from six random field views), on the other hand the mean value of Vickers microhardness was calculated 109.8HV and 167.8HV (absolute error ±1HV) for these axes respectively. Many more samples and measurements would be needed in order to determine a reliable mathematical relation between porosity and microhardness.

Keywords: Albanian-Dalmatian axe, celt axe, porosity, Vickers microhardness, production process.

Introduction

The Albanian-Dalmatian axes appeared at the end of the Bronze Age (XIII-X century B.C.). Their shape has oriental origin and it is thought that they were produced in the northern Albania. The celts began to appear in Northern Albania in the XII century B.C. and is believed that their production was influenced by the Pannonia-Balkan invasion. These axes have various shapes and in many cases they were found in tombs together with imported Helladic ceramics or other materials from the Aegean culture. Both types groups of objects are believed to be local productions. (Prendi, 1958; Prendi, 2008; Prendi, 2008). According to Çakaj *et al.* these axes resulted tin bronzes with Pb content less than 2%. The possibility to remove samples from these axes was restricted because they were exposed in the

Museum of Shkodra. The ideal scenario would have been to remove samples from different areas of the object, such as: cutting edge, centre of shaft, near the socket, etc. But since this was not allowed the sample removing process was reduced to one exemplar for each group of axes and in the less visible part of the object. However the microstructure of the removed samples resulted composed by straight dendrites leading to the conclusion of a possible casting process as the final stage of production. (Çakaj *et al.*, 2016)

The aim of this paper is to study the effect of structure porosity in the microhardness values of the axes samples.

Human civilization as we know it would not have been possible without metal casting. It must have emerged from the darkness of antiquity first as magic, later to evolve as an art, then as a technology, and finally as a complex interdisciplinary science. The appearance of plasters and ceramics in the Neolithic period is evidence that the use of fire was being extended to materials other than stone. Exactly when the casting of metals began is not known. Archaeologists give the name Chalcolithic to the period in which metals were first being mastered and the date this period, which immediately preceded the Bronze Age, very approximately to between 5000 and 3000 B.C. Analyses of early cast axes and other objects give chemical compositions consistent with their having been cast from native copper and are the basis for the conclusion that the melting of metals had been mastered before smelting was developed. The furnaces were rudimentary. It has been shown by experiment that it was possible to smelt copper, for example, in a crucible. Nevertheless, the evidence for casting demonstrates an increasing ability to manage and direct fire in order to achieve the required melting temperatures. The fuel employed was charcoal, which tended to supply a reducing atmosphere where the fire was enclosed in an effort to reduce the loss of heat. The molds were mainly of stone. The tradition of stone carving was longer than any of the pyrotechnologies, and the level of skill allowed very finely detailed work. The stone carved was usually of a smooth texture such as steatite or andesite, and the molds produced are themselves often very fine objects, which can be viewed in museums. (ASM Special Handbook, 2001; ASM Metals HandBook Volume 15, 2008; Scott, 2011)

Porosity occurs in cast metals due to negative pressures generated during solidification contraction, and pressure developed by gases dissolved in the molten metal. These processes can act together or separately in order to produce shrinkage or gas defects (pores). In homogeneous liquid the formation of pores occur without being influenced by impurities and/or external surfaces. Meanwhile the opposite happens during heterogeneous nucleation where pores are formed because of the impurities present in the melt and/or gas bubble surfaces, inclusions, mold walls, crevices, etc. Since the pore surface serve as strain amplification site the object microhardness values should decrease with the increment of pore percentage. (Gupta *et al.*, 1992; ASM Metals HandBook Volume 8, 2000)

Materials and methods

Figure 1 shows where the sample was taken from the Albanian-Dalmatian axe no. 14745 and the celt no. 14757, along with the corresponding sketches. (Çakaj *et al.*, 2016)

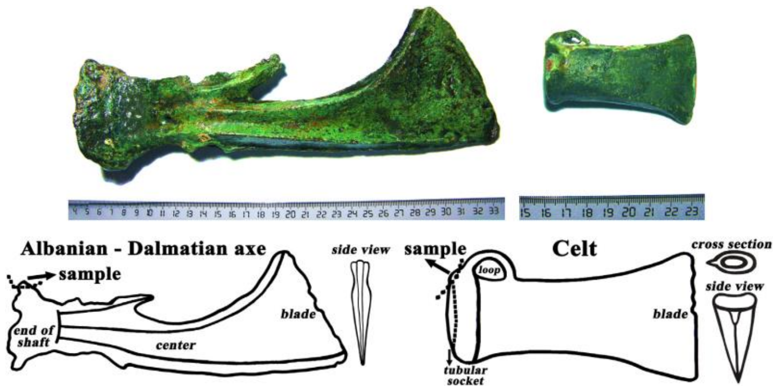

Figure 1. The Albanian-Dalmatian axe no. 14745 and the celt no. 14757 (above), the axes sketches along with the position where the sample was taken; the celt's socket cross section and side view (below). (Çakaj *et al.*, 2016)

Image analysis was performed for both samples. Six random microstructure photos were obtained with Sonny TCC-8.1 digital camera attached to Kozo XJP304 microscope and they were examined using View-7 image analysis software.

The light reflected from the pores on the sample surface is scattered making them appear black. Meanwhile the alloy surface appears bright since the reflected light reaches the microscope oculars. This difference in brightness and color is used by the image analysis software to divide the pores from the alloy in the photo. The percentage of the pore surface is calculated as the ratio of the dark surface over the total photo surface. In the same way is proceeded for the alloy percentage. (User manual View-7)

The results of the pore percentage were confronted with the microhardness values according to Çakaj *et al*.

Results and discussions

Table 1 shows the microhardness values according to Çakaj *et al.* while the image analysis results for the pore and alloy surface percentages are presented in table 2. Figure 2 shows the photos (magnification 100X) examined with View-7 image analysis software for both samples.

Table 1. The Vickers microhardness test results and the calculated mean value for both axes samples (absolute error ±1HV). (Çakaj *et al.*, 2016)

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	HV_{mean}
Alb.-Dal. axe sample	170	151	172	166	160	188	167.8
Celt sample	116	106	109	104	114	110	109.8

Table 2. Image analysis results for the pore and alloy surface percentages, for both samples.

Albanian-Dalmatian axe sample			**Celt axe sample**		
% of pores	**% of error**	**% of alloy**	**% of pores**	**% of error**	**% of alloy**
2.4	0.08	97.6	8.7	0.09	91.3
3.7	0.2	96.3	7.2	0.09	92.8
2	0.1	98	9.5	0.08	90.5
0.9	0.07	99.1	8.5	0.09	91.5
2.4	0.1	97.6	9.5	0.1	90.5
1.1	0.08	98.9	9.2	0.09	90.8
Mean % of pores = 2.08			**Mean % of pores = 8.76**		
Mean % of error = 0.105			**Mean % of error = 0.09**		
Percentage of pores 2.08% ± 0.105%			**Percentage of pores 8.76% ± 0.09%**		

The mean Vickers microhardness value for the Albanian-Dalmatian axe sample is 167.8HV while for the celt sample is 109.8HV. From the image analysis performed in this study the mean pore percentage for the first axe sample resulted 2.08% and 8.76% for the second one.

a)

b)

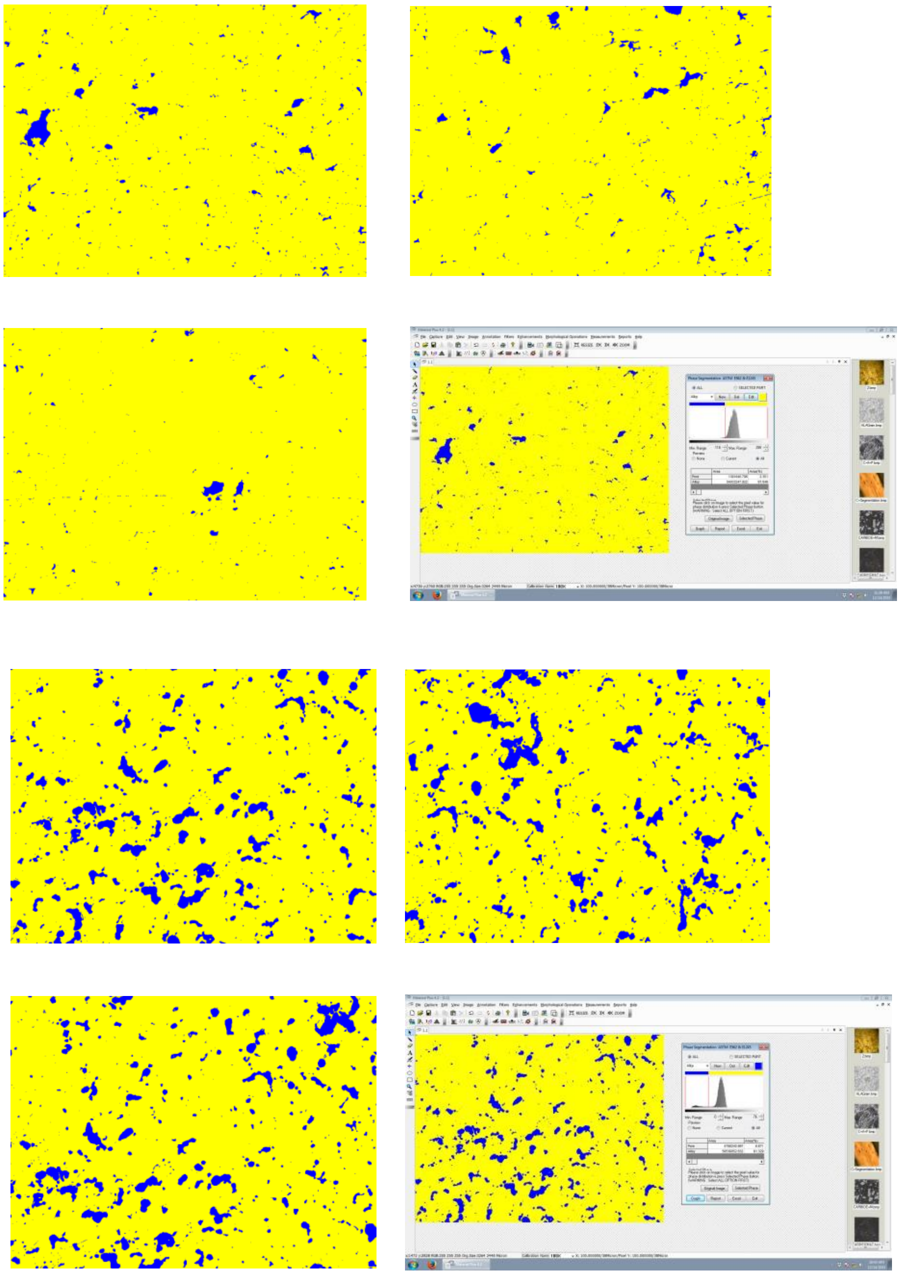

Figure 2. Three of the photos (magnification 100X) examined with View-7 image analysis software for the a) Albanian-Dalmatian axe sample and b) celt axe sample. Pores and alloy differ in colors (pores are blue, the alloy is yellow) which can be chosen in the software settings.

Conclusions

Taking into account that both microstructure samples contained straight dendrites can lead to the conclusion that casting was the final step of production. The creation of pores during casting is due to negative pressures generated from solidification contraction, and pressure developed by gases dissolved in the molten metal. The difference in the Vickers mean value between the Albanian-Dalmatian axe sample and the celt one is 58HV. While from the image analysis the second axe sample has a pore percentage around 4.2 times higher than the first one. Pores serve as strain concentration sites making the alloy less resistant to external forces explaining the decrease of the microhardness value with the increment of the structure pore percentage.

References

ASM Metals HandBook Volume 15 (2000): Mechanical Testing and Evaluation. ISBN 0-87170-389-0

ASM Metals HandBook Volume 8 (2008): Casting. ISBN: 978-0-87170-711-6.

ASM Special Handbook (2001): Copper and Copper alloys. ASM International, USA, ISBN: 0-87170-726-8: 77, 360-363

Çakaj O., Dilo T., Civici N., Schmidt G., Stamati F. (2016): Study of eight Albanian-Dalmatian axes (XIII-XII B.C.) and six celts (XI-X B.C.) found in northern Albania, by µ-XRF, OM, SEM-EDS. Journal of Archaeological Science: Reports, vol. 9: 219–225

Gupta A. K., Saxena B. K., Tiwari S. N., Malhotra S. L. (1992): Review – Pore formation in cast metals and alloys. Journal of Materials Sciences, 27: 853-862

Prendi F. (1958): Materiale të kulturës ilire të zbulueme në Shqipërinë e veriut. BUSHT, Albania: 110-132

Prendi F. (2008): Chapter 5: The Prehistory of Albania. In: Boardman J., Edwards I. E. S., Hammond N. G. L., Sollberger E., (Eds.) (2008): The Cambridge ancient history, vol. III, part 1: The Prehistory of the Balkans; The middle east and the Aegean world, X to VIII centuries B.C. Cambridge University Press. ISBN 0521 22496 9

Prendi F. (2008): Studime Arkeologjike. ARK-KOS, Kosova: 453-474.

Scott D. A. (2011): Ancient metals: microstructure and metallurgy volume I. Conservation Science Pres, ISBN: 9780982933800: 137-260.

User manual View-7