Table 2. Measured and calculated mean values of the Vickers micro hardness test (for the rhombic trace diagonal Δd=0.5 μm).

Object	Vickers micro hardness								$\overline{HV}$
	Test 1	Test 2	Test 3	Test 4	STest 5	Test 6	Test 7	Test 8	
Necklace (small bead)	122	130	130	127	123	133	-	-	127.5
Belt application	105	94.9	104	101	95.8	96.7	104	106	100.9
Button	142	121	119	117	121	140	-	-	126.6

$\overline{HV}$, hardness value.

low (<17%) and high (>17%) tin bronzes. Theoretically, 17% is the maximum tin content that can be completely dissolved in copper, practically this percentage can be around 14%. The button is a low tin bronze where the centre of the dendrites is rich in copper because of the higher melting temperature. The dendrites growth is achieved by tin deposits and for tin bronzes with around 10% Sn, similar to the button sample, the dendrites are surrounded by + eutectoid. The low content of lead in the button makes the alloy hard to cast and the dendrites presence in the microstructure suggests that it might have been indeed casted. The very thin button build suggests that the mold was sophisticated in order to produce a low lead object. This could have been a rare occurrence taking into account the button dating. Adding lead in copper alloys, like in the necklace and belt application cases, lowers the alloy melting temperature and makes the casting process easier although this element is almost insoluble in copper. The low Sn percentage in the belt application suggests that this element could be absorbed completely in the dendrites growth. However, this depends significantly from the cooling rate, meaning that at a low cooling rate the equilibrium and tin absorption are more likely to occur. The small bead of the necklace cannot have homogeneous microstructure phase because of the high tin content, which in theory is no longer completely soluble in copper. These alloys are usually unworkable and can only be casted (Scott, 1991).

Conclusions

From the XRF analysis that was performed on the samples, the button turns out to be a copper-tin alloy, while the necklace and the belt application are composed mainly of copper-tin-lead. Iron, zinc and calcium can be contaminations from the soil, being typical plant nutrition chemical elements. Arsenic and nickel can indicate a prehistoric alloy. From the corrosion microscope photos it is clear that the ornamental accessories are authentic and not fake replicas. The dendritic microstructure indicates that the necklace, the belt application and the button might have been produced from a cast process in moulds with no further working. The necklace and the button, having a light tin content, result with the highest Vickers micro hardness values among the three samples. In fact, the belt application has a 20% lower micro hardness value compared to the necklace and button, which could be explained with its higher lead content and lower tin percentage.

References

Boardman J, Edwards IES, Hammond NGL, Sollberger E, 1982. The Cambridge ancient history. The Prehistory of the Balkans, the Middle East and the Aegean world, tenth to eighth centuries BC. Cambridge University Press, Cambridge, UK.

Ceka N, 2000. Përpara se të shkruhej historia. In: N. Ceka (ed.) Ilirët. SHBLU Publ., Tirana, Albania, pp 36-7.

Domenech-Carbo A, Domenech-Carbo MT, Martinez-Lazaro I, 2008. Electrochemical identification of bronze corrosion products in archaeological artefacts. A case study. Microchim Acta 162:351-9.

Domenech-Carbo A, Domenech-Carbo MT, Trinidad P, Bouzas MC, 2011. Application of modified Tafel analysis to the identification of corrosion products on archaeological metals using voltammetry of microparticles. Electroanalysis 23:2803-12.

Jacques EE, 1995. The Albanians: an ethnic history from prehistoric times to the present. McFarland & Company Inc., Jefferson, NC, USA.

Mircea O, Sandu I, Vasilache V, Sandu AV, 2012. Study of the atypical formations in the corrosion bulks of an ancient bronze shield, by optical and electron microscopy. Microsc Res Techniq 75:1467-74.

MIT, 2003. The metallographic examination of archeological artifacts, laboratory manual. Massachusetts Institute of Technology ed., Cambridge, MA, USA.

Potts P, West M, 2008. Portable x-ray fluorescence spectrometry capabilities for in situ analysis. The Royal Society of Chemistry ed., London, UK.

Pracejus B, 2008. The ore minerals under the microscope, an optical guide. Elsevier, Amsterdam, The Netherlands.

Prendi F, 1958. Materiale të kulturës ilire të zbulueme në Shqipërinë e veriut. Bul Univ Shtet Tirane 2:110-32.

Prendi F, 1977-1978. Epoka e bronzit në Shqipëri. Iliria 7-8:5-58.

Prendi F, 2008. Studime arkeologjike. ARKKOS, Pristina, Kosovo.

Sandu I, Mircea O, Sandu AV, Vasilache V, Sandu IG, 2014. Study of the Liesegang chemical effects in antique bronze artefacts during their stay within an archaeological site. Available from: http://www.revistadechimie.ro/article_eng.asp?ID=3980

Sandu I, Mircea O, Vasilache V, Sandu I, 2012. Influence of archaeological environment factors in alteration processes of copper alloy artifacts. Microsc Res Techniq 75:1646-52.

Sandu I, Ursulescu N, Sandu IG, Bounegru I, Sandu ICA, Alexandru A, 2008. Pedological stratification effect of corrosion and contamination products on Bysantine bronze artefacts. Corros Eng Sci Techn 43:256-66.

Scott DA, 1991. Metallography and microstructure of ancient and historical metals. Tien Wah Press, Singapore.

Tylecote RF, 1992. A history of metallurgy. Antony Rowe Ltd., Croydon, UK.

Vink BW, 1986. Stability relations of malachite and azurite. Mineral Mag 50:41-7.

Wayne R, 2009. Light and video microscopy. Elsevier, Amsterdam, The Netherlands.