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PONOVNA KONZERVATORSKO-RESTAURATORSKA OBRADA PRAPOVIJESNE KACIGE

RE-CONSERVATION-RESTORATION TREATMENT OF A PREHISTORIC HELMET

U članku se opisuje konzervatorsko-restauratorska obrada prapovijesne kacige koja je stigla u Arheološki muzej Zadar kao razmjena s muzejom u Anconi još u vrijeme prije Drugog svjetskog rata. Opisane su sve faze rada s kratkim osvrtom na korozijske promjene koje su se dogodile na kacigi tijekom vremena pohranjivanja. Date su preporuke za njezino čuvanje.

Ključne riječi: korozija bronce, konzervatorsko-restauratorska obrada, aktivna kloridna korozija, prapovijesna kaciga

The article describes the conservation and restoration treatment of a prehistoric helmet that arrived at the Zadar Museum of Archaeology as an item exchanged with the museum in Ancona back at a time before World War II. It describes all phases of work with a brief overview of corrosion changes that occurred over time during which the helmet was stored. Recommendations are given for its preservation.

Keywords: corrosion of bronze, conservation and restoration treatment, active chloride corrosion, prehistoric helmet

Slika 1. Kaciga prije konzervatorsko-restauratorske obrade
Figure 1. The helmet before conservation and restoration treatment.
foto / photo: **J. Lovrić**

Osnovni podatci o predmetu

Prapovijesna kaciga potječe iz Južne Italije (Picenum), a datirana je u starije željezno doba. Budući da ovakvih kaciga nema na našim prostorima, pretpostavlja se da je u Arheološki muzej Zadar stigla kao razmjena s muzejom u Anconi još u vrijeme prije Drugog svjetskog rata.[1] O njoj nemamo nikakve podatke, jer je dokumentacija Muzeja izgorjela u požaru za vrijeme Drugog svjetskog rata. Kaciga je vjerojatno brončana[2] s kompozitnom kalotom i obodom. Sastavljena je od 4 ploče brončanog lima spojene zakovicama. Petu ploču čini široki obod ukrašen biljnim motivima tehnikom iskucavanja. Na vrhu kalote su dva elementa od lijevane bronce, a pri dnu kuka i ušica. Lijevani elementi su služili za pričvršćivanje perjanice.

Opis zatečenog stanja predmeta

Kaciga je pri dolasku iz Italije bila restaurirana. Poprečne ploče i veći dio oboda je originalan, a ostale ploče su rekonstruirane. Kaciga je na obradu donesena u prilično lošem stanju (Sl. 1). Vidljiva su značajna oštećenja na rekonstruiranim dijelovima, kao i tragovi aktivne kloridne korozije na metalnim dijelovima. Bila je prekrivena debelim slojem prašine. Cijela unutrašnjost kacige bila je obložena čeličnom mrežom, a rub oboda s donje strane pojačan debljom čeličnom žicom koja je bila pričvršćena lemom. Mreža se većim dijelom sjedinila s masom kojom je kaciga rekonstruirana, a dio mreže koji nije bio stopljen s masom je na nekoliko mjesta korodirao. Žica s donje strane

1 Kaciga i ostali predmeti koji su pristigli kao razmjena su u postupku obrade.
2 Vjerojatno se radi o bronci u užem smislu te riječi tj. slitini bakra i kositra te bi za egzaktan podatak o sastavu materijala trebalo provesti prikladnu analizu.

Basic facts about the artefact

The prehistoric helmet originates from Southern Italy (Picenum), and dates back to the early Iron Age. As there are no such helmets in our region, the assumption is that it arrived at the Zadar Museum of Archaeology as an exchanged item with a museum in Ancona in the period before World War II.[1] There is no information on the artefact whatsoever, since the Museum's documentation was destroyed by fire during World War II. The helmet is probably made of bronze[2] with a composite dome and rim. It is composed of four bronze panel sections that are riveted. The fifth panel provides a wide brim decorated with embossed floral motifs. At the top of the dome are two cast bronze components, and the bottom has a hook and eyelet. Cast components are used for fastening feathers.

Description of the current state of the object

The helmet was restored before its arrival from Italy. The transverse plates and larger part of the rim is original, whereas the other panels were reconstructed. The helmet was brought in for restoration in a relatively poor condition (Fig. 1). Significant damage to the reconstructed parts are evident, as well as traces of active chloride corrosion on the metal parts. The helmet was covered with a thick layer of dust. The entire interior section of the helmet was covered with a steel mesh while the rim edge on the bottom side was reinforced with a thick steel wire fastened with a solders. The mesh is largely connected to the main section of which the helmet is reconstructed, and part of a mesh that was not blended with main section has corroded in several places. The wire from the underside of the rim was corroded, cracked and warped. The reconstructed part of the rim was also cracked, with the original section completely separated from the dome. One part is missing.

Brief overview of changes due to corrosion

In the corrosion process, the metal surfaces became covered with a layer of cuprous oxide, known as cuprite (Cu_2O) and are a red colour. This oxide layer was covered with a dark green copper carbonate, malachite ($Cu_2(OH)_2CO3$) or less frequently with a blue copper carbonate, azurite ($Cu_3(OH)_2(CO_3)_2$).[3] Malachite and azurite create a noble patina.

1 The helmet and other items that arrived as an exchange item are in the process of being treated.
2 It probably is bronze in the strict sense of the word, i.e. an alloy comprising of copper and tin, whereas exact information on the material composition would require a proper analysis.
3 R. B. Faltermeier, 1998, 49.

Slika 2. Tragovi aktivne kloridne korozije na kacigi
Figure 2. Traces of active chloride corrosion on the helmet.
foto / photo: **J. Lovrić**

oboda je korodirala, pukla i deformirala se. Rekonstruirani dio oboda je bio ispucan, a originalni dio potpuno odvojen od kalote. Jedan dio je nedostajao.

Kratak osvrt na korozijske promjene

U korozijskom procesu površina metala se prekriva slojem kupro-oksida koji je poznat pod nazivom kuprit (Cu_2O) i crvene je boje. Ovaj sloj oksida se prekriva tamnozelenim bakrenim karbonatom, malahitom ($Cu_2(OH)_2CO_3$) ili manje učestalim plavim bakrenim karbonatom, azuritom ($Cu_3(OH)_2(CO_3)_2$.[3] Malahit i azurit čine plemenitu patinu. Plemenita patina je ravnomjerno raspoređena po površini predmeta, jasno ocrtava sve detalje i štiti metal od daljnjeg propadanja. Promjene se opažaju u prisutnosti kloridnih iona koji pospješuju koroziju, jer migriraju kroz oksidni sloj i formiraju bijeli voštani sloj kupro-klorida (CuCl), nantokita na površini korodirajućeg metala. Nantokit je stabilan sve dok nema vlage i kisika i kao takav može ostati zapečaćen ispod slojeva korozije bez da uzrokuje oštećenja. U prisutnosti vlage i kisika on reagira ekstremno brzo.[4] Dolazi do njegove hidrolize i stvara se kloridna kiselina i kupri-klorid ($CuCl_23Cu(OH)_2$ tzv. paratakamit. Paratakamit je spoj koji se na površini bronce opaža kao blijedo zelena prašnjava patina (Sl. 2). Nastala kloridna kiselina nagriza metal što rezultira dodatnim stvaranjem kupro-klorida, nantokita. Proces se ciklički nastavlja dok se metal ne raspadne.[5] Ukoliko u bronci nisu prisutni kloridi ova se pojava neće dogoditi ni pri uvjetima ekstremne vlažnosti. S obzirom da nisu provedene analize korozijskih produkata, kao ni sastav slitine, ovo je samo teoretski prikaz korozijskih promjena.

Konzervatorsko-restauratorska obrada kacige odvijala se u nekoliko faza:

1. Čišćenje
2. Stabilizacija
3. Lijepljenje i rekonstrukcija
4. Nanošenje zaštitnih premaza

Čišćenje

Kaciga je očišćena mehanički. Kako je već ranije bila konzervirana, složeniji konzervatorski zahvati po pitanju čišćenja nisu bili potrebni. Bilo je potrebno ukloniti debele naslage prašine i sanirati mjesta na kojima se pojavila aktivna kloridna korozija. Korišteni su ručni alati poput skalpela i rotacijskog mikromotora.[6] Kaciga je

3 R. B. Faltermeier, 1998, 49.
4 M. Cronyn, 1990, 218-219, 226-227.
5 L. D. Hamilton, 1999, FILE 12.
6 U osovinu mikromotora stavljala su se glodala od aluminijevog-oksida.

The noble patina is evenly distributed over the artefact's surface, clearly outlining all the details and protecting the metal from further deterioration. Changes are observed with the presence of chloride ions, which promote corrosion, because they are transferred through the oxide layer, forming a white waxy layer of cuprous chloride (CuCl), a nantokite on the surface of the corroding metal. The nantokite is stable while there is no moisture and oxygen, and as such may remain sealed under layers of corrosion without causing damage. In the presence of moisture and oxygen, it reacts extremely quickly,[4] leading to its hydrolysis and creating a hydrochloric acid and cupric chloride ($CuCl_23Cu(OH)_2$, so called paratacamite. Paratacamite is a compound found on the surface of bronze as a pale green powdery patina (Fig. 2). The resulting hydrochloric acid corrodes the metal leading to the further formation of cuprous chloride, nantokite. The process is cyclic and continues until the metal falls apart.[5] If the bronze does not contain chlorides, this phenomenon will not occur even under conditions of extreme humidity. Since an analysis of the corrosive elements has not been carried out, the composition of alloys here is just a theoretical view of possible corrosive changes.

The conservation and restoration treatment of the helmet took place in several stages:

1. Cleaning
2. Stabilisation
3. Bonding and reconstruction
4. Applying a protective primer

Cleaning

The helmet was hand-cleaned. Since it was already conserved previously, more complex conservation work on cleaning it was not deemed necessary. It was necessary though to remove thick layers of dust and repair sections where active chloride corrosion had occurred. Hand tools were used such as scalpels and a rotary micromotor.[6] The helmet was micro

4 M. Cronyn, 1990, 218-219, 226-227.
5 L. D. Hamilton, 1999, FILE 12
6 An aluminium oxide milling tool is placed into the micromotor shaft.

Slika 3. Kaciga u postupku lijepljenja i rekonstrukcije
Figure 3. The helmet in the sealing and reconstruction process.
foto / photo: **J. Lovrić**

mikropjeskarena staklenim granulatom (70 – 110 µm), koji osim što čisti, ujedno i polira površinu predmeta. Postupak mikropjeskarenja se odvijao oprezno pri niskom tlaku kako se ne bi oštetila plemenita patina koja je na kacigi ostala dobro sačuvana. Veliki problem predstavljala je žica na obodu i mreža kojom je unutarnji dio kacige bio obložen. Žica i dio mreže s oboda su u potpunosti uklonjeni, dok je mrežu s unutarnje strane kalote bilo teško ukloniti jer se sjedinila s masom kojom je restaurirana. Procijenjeno je da bi njeno potpuno uklanjanje izazvalo urušavanje cijele kalote, pa je kao takva ostavljena. Mjesta na kojima je mjestimično korodirala su očišćena mehanički.

Stabilizacija

Kaciga je aktivno stabilizirana srebrnim oksidom zbog vidljivih znakova aktivne kloridne korozije. Mjesta zahvaćena aktivnom kloridnom korozijom su sondirana i u sondirana mjesta je špatulom nanesen srebrni oksid ovlažen etanolom. Kaciga je izložena utjecaju vlage na način da je stavljena u hermetički zatvorenu posudu (eksikator) u kojoj su uvjeti visoke vlažnosti postignuti zasićenom otopinom natrij-tiosulfata-pentahidrata. Nantokit (kupro-klorid) reagira sa srebrnim osidom i stvara stabilne soli kupro-oksida i srebrni klorid koji nepropusno zatvara od vlage ostale kupro-kloride. Postupak se ponavlja dokle god se na površini uočavaju zelene mrlje.[7]

Lijepljenje i rekonstrukcija

Manji ulomci s oboda kacige su lijepljeni trenutnim ljepilom na bazi cijanoakrilata, a teži element od lijevane bronce pričvršćen je na vrh kacige dvokomponentnim

7 M. Klarić, 1998, 65.

sand-blasted using a glass granulate (70-110 microns), which besides cleaning also polishes the surface of artefact. The procedure involving micro-abrasive sandblasting was carefully carried out at a low pressure to avoid damaging the noble patina that remained well preserved on the helmet. The bigger problem was the wire on the rim and the mesh used to cover the inner part of the helmet. The wire and mesh were completely removed from the rim, while the mesh was difficult to remove from the inside of the dome because it was fused to the main section with which it was restored. Assessments indicated that its removal would cause the complete collapse of the entire dome, and was therefore left untouched. Places that were partly corroded were hand-cleaned.

Stabilisation

The helmet was actively stabilized using silver oxide due to the visible signs of active chloride corrosion. Places affected by active chloride corrosion were probed and the probed places had silver oxide moistened with ethanol applied to them with a spatula. The helmet was exposed to moisture by placing it in an airtight container (desiccator) in which high humidity conditions were attained using a saturated solution of sodium thiosulfate pentahydrate. Nantokite (cuprous chloride) reacted with the silver oxide and formed a stable salt containing cuprous oxide and silver chloride, sealing against the moisture content of other cuprous chloride. The procedure was repeated until green spots were observed on the surface.[7]

Bonding and reconstruction

Smaller fragments from the helmet rim were glued using a cyanoacrylate instant adhesive, where the heavier cast bronze element was attached to the top of the helmet with a two-component epoxy adhesive. The missing parts were reconstructed using a two-component epoxy resin Araldite 427 and green pigment was added (Fig 3). After drying, the surface was grinded into the appropriate shape. Earlier reconstructed parts were coated using an acrylic paint with the addition of a copper pigment for consolidating the area. The metal helmet parts were polished with brushes made of synthetic materials.

Applying protective coatings

The helmet was impregnated with a 2% solution of Paraloid 72B in ethyl acetate. Paraloid 72B is a thermoplastic acrylic

7 M. Klarić, 1998, 65.

Slika 4. Kaciga nakon konzervatorsko-restauratorskog zahvata
Figure 4. The helmet after conservation and restoration work.
foto / photo: **J. Lovrić**

epoksidnim ljepilom. Nedostajući dijelovi su rekonstruirani dvokomponentnom epoksidnom smolom Araldit 427 uz dodatak zelenog pigmenta (Sl. 3). Nakon sušenja površina je oblikovana brušenjem. Ranije rekonstruirani dijelovi su premazani akrilnom bojom uz dodatak bakrenog pigmenta radi konsolidacije površine. Metalni dijelovi kacige su polirani četkicama od umjetnih materijala.

Nanošenje zaštitnih premaza

Kaciga je impregnirana 2%-tnom otopinom Paraloida 72B u etil-acetatu. Paraloid 72B je termoplastičana akrilna smola koja se široko upotrebljava u restauratorskoj struci za premazivanje, učvršćivanje i kao ljepilo. Kod pripreme otopine važno je pripremiti otopinu odgovarajuće koncentracije, jer se u radu s visokim koncentracijama površina metala može zasjajiti. Takav sjajan izgled metala nije nam poželjan.

Preporuke za čuvanje brončanih predmeta

Ukoliko su brončani predmeti kontaminirani kloridnim ionima, ključni faktor za razvoj aktivne kloridne korozije je relativna vlažnost. Provedene su mnoge studije kojima se pokušala odrediti kritična vrijednost relativne vlažnosti pri kojoj dolazi do razvoja aktivne kloridne korozije.[8] Iskustveni podaci nam ukazuju da se rizik za pojavu aktivne kloridne korozije javlja i raste iznad vrijednosti od 42% RH, dok iznad vrijednosti 68% brzina korozijske reakcije rapidno raste. Iznad te vrijednosti brončani predmeti se ne bi trebali izlagati. Inhibitorima korozije se nastoji zaustaviti razvoj aktivne kloridne korozije, međutim dokazano je da se i nakon njihove primjene (npr. benzotriazolom) korozija može nastaviti. Stoga ukoliko se na predmetima pojave znakovi aktivne kloridne korozije, relativna vlažnost se treba smanjiti ispod 42% .[9]

Zaključak

Kaciga je iznimno vrijedan i zanimljiv nalaz. Zanimljiva je iz dva razloga. Prvi je što takvih kaciga nema na našim prostorima, a drugi je način na koji je restaurirana. Iako su u izboru materijala za restauraciju bili korišteni neki potpuno

resin widely used in the restoration profession for applying coatings, stiffening and as an adhesive. In preparing the solution, solution should be prepared at the appropriate concentration, because when working with high concentrations, the metal surface can attain a gloss. This kind of gloss appearance of the metal is what is not desired.

Recommendations for preserving bronze artefacts

If bronze artefacts are contaminated with chloride ions, the key factor for the onset of active chloride corrosion is relative humidity. Numerous studies have been conducted that have sought to determine the critical value of relative humidity at which the onset of active chloride corrosion occurs.[8] Empirical data has shown that the risk of the onset of active chloride corrosion occurs and increases when the RH value exceeds 42%, whereas when exceeding 68% the intensity of corrosive reactions increases rapidly. Bronze items should not be exposed to conditions above this value. Corrosive inhibitors endeavour to halt the onset of active chloride corrosion; however, it has been proven that even after their application (e.g. benzotriazole), corrosion may continue. Therefore, if the artefacts show signs of active chloride corrosion, the relative humidity should be reduced to below 42%.[9]

8 Prema jednoj studiji, relativna vlažnost od 42 - 46% je adekvatna za čuvanje mnogih brončanih predmeta i pri toj vlažnosti kupro-kloridi se neće podvrći kemijskim reakcijama (D. A. Scott, 1990, 193-206). Prema drugoj studiji kritična vrijednost RH za razvoj aktivne kloridne korozije je 63%. Kako se ipak radi samo o podatcima dobivenim u laboratoriju, predlaže se čuvanje bakra i bakrenih slitina pri RH nižoj od 60%. To znači da će kloridno kontaminirani predmeti od bakrenih slitina biti sigurni i neće zahtijevati nikakve tretmane u uvjetima relativne vlažnosti od 45 - 60% (A. Papapelekanos, 2010, 50).

9 M. Rimmer – D. Thickett – D. Watkinson – H. Ganiaris, 2013, 11-12.

8 According to one study, a relative humidity of 42-46% is adequate for preserving many bronze artefacts and at this humidity the cuprous-corrida will not undergo chemical reactions (D. A. Scott, 1990, 193-206). According to another study, the critical value of RH for the onset of active chloride corrosion is 63%. Since this data has been acquired in the laboratory, the recommendation is that copper and copper alloys be preserved at a RH lower than 60%. This means that chloride-contaminated artefacts made of copper alloys will be safe and will not require any treatment when conditions for relative humidity are 45-60% (A. Papapelekanos, 2010, 50).

9 M. Rimmer – D. Thickett – D. Watkinson – H. Ganiaris, 2013, 11-12.

neprimjereni materijali poput metalne žice kojom je bila obložena, treba uzeti činjenicu da je to bilo davno u vrijeme prije Drugog svjetskog rata. Bez obzira na sve to, nepoznati restaurator ju je uspio sačuvati od propadanja, a ponovnom konzervatorsko-restauratorskom obradom vraćen joj je prvobitni izgled i sjaj. Važno ju je ubuduće čuvati u uvjetima kontrolirane vlažnosti. Samo na takav način ju možemo sačuvati za buduće generacije.

Conclusion

The helmet is an exceptionally valuable and interesting find, and is so for two reasons. The first is that there are no such helmets in our region, and second is the way it was restored. Although the choice of some materials for the restoration were totally inappropriate, such as metal wire used to cover it, the fact should be taken into consideration that this was undertaken long ago in the period before World War II. Regardless of all this, the unknown restorer had succeeded in preserving it from decay, and the re-conservation-restoration procedure returned it to its original appearance and lustre. It is now important to preserve it in the future under controlled humidity conditions. Only in this way will we preserve it for future generations.

Literatura / Bibliography

Cronyn, J. M.,1990 – *The Elements of Archaeological Conservation*, London, 1990.

Faltermeier, R.B., 1997 – Corrosion inhibitor testing in archaeological conservation, *Archaeology International,* 1, 1997, 49-50.

Hamilton, D. L., 1999 – *Methods of Conserving Archaeological Material from Underwater Sites*, Texas A&M University, 1999.

Klarić, M., 1998 – *Uvod u konzervaciju kovina*, Pomorski muzej Split, 1998.

Papapelekanos, A., 2010 – The Critical RH for the Appearance of „Bronze Disease" in Chloride Contaminated Copper and Copper Alloy, *Artefacts, e-conservation magazine*, 13, 2010, 43-52.

Rimmer, M. – Thickett, D. – Watkinson, D. – Ganiaris, H., 2013 – *Guidelines for the Storage and Display of Archaeological Metalwork*, Swindon, Englis Heritage, 2013.

Scott, D. A., 1990 – Bronze Disease: A Review of Some Chemical Problems and the Role of Relative Humidity, *Journal of The American Institute for Conservation*, 29 , no. 2, 1990, 193-206.