MC95
Proceedings of the International Metallography Conference
Colmar, France, 10-12 May 1995

Organized by
The Council of ASM International Europe
The Metallography Technical Division
The International Metallographic Society

Manager Book Acquisitions
Veronica Flint

Manager Book Production
Grace M. Davidson

Production Project Coordinator
Cheryl L. Powers
No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the written permission of the copyright owner.

Great care is taken in the compilation and production of this Volume, but it should be made clear that NO WARRANTIES, EXPRESS OR IMPLIED, INCLUDING, WITHOUT LIMITATION, WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, ARE GIVEN IN CONNECTION WITH THIS PUBLICATION. Although this information is believed to be accurate by ASM, ASM cannot guarantee that favorable results will be obtained from the use of this publication alone. This publication is intended for use by persons having technical skill, at their sole discretion and risk. Since the conditions of product or material use are outside of ASM's control, ASM assumes no liability or obligation in connection with any use of this information. No claim of any kind, whether as to products or information in this publication, and whether or not based on negligence, shall be greater in amount than the purchase price of this product or publication in respect of which damages are claimed. THE REMEDY HEREBY PROVIDED SHALL BE THE EXCLUSIVE AND SOLE REMEDY OF BUYER, AND IN NO EVENT SHALL EITHER PARTY BE LIABLE FOR SPECIAL, INDIRECT OR CONSEQUENTIAL DAMAGES WHETHER OR NOT CAUSED BY OR RESULTING FROM THE NEGLIGENCE OF SUCH PARTY. As with any material, evaluation of the material under end use conditions prior to specification is essential. Therefore, specific testing under actual conditions is recommended.

Nothing contained in this book shall be construed as a grant of any right of manufacture, sale, use, or reproduction, in connection with any method, process, apparatus, product, composition, or system, whether or not covered by letters patent, copyright, or trademark, and nothing contained in this book shall be construed as a defense against any alleged infringement of letters patent, copyright, or trademark, or as a defense against liability for such infringement.

Comments, criticisms, and suggestions are invited, and should be forwarded to ASM International.

Library of Congress Catalog Card Number: 96-83615
ISBN: 0-87170-569-9
SAN: 204-7586

ASM International®
Materials Park, OH 44073-0002
Printed in the United States of America
Archeometallurgical Examination of Bronzes from the Second Iron Age

F.J. Sarabia-Herrero, C. Sanz-Minguez, G. Delibes-de-Castro, J. Martín-Gil
University of Valladolid, Spain

ABSTRACT

The present paper is part of an archeometallurgical examination of Vaccei bronzes from the archaeological place of Las Ruedas (Padilla de Duero, Valladolid, Spain). A sample of 6 objects is discussed here as representative of the main results from the metallographic examination, showing high skill in the forge work compensating foundry problems. It is observed that those problems for melting bronze decrease gradually being still important till the beginning of the Roman Conquest, when a real advance in the casting techniques can be recorded.

The pictures shown here can be regarded as examples of the technical problems arising when handing archaeological material. As there was no authorization for cutting or mounting the objects for metallographic examination due to legal restrictions, they had to be held by hand and polished only on their outer surfaces, the consequence being that pictures show many scratches and marks left during the polishing process.

INTRODUCTION

All the objects considered here come from modern archaeological excavation (1) of cremation graves found in Las Ruedas (Padilla de Duero, Valladolid, Spain), placed by the river Duero (2). It is dated in the Iron Age II, during the last five centuries BC, and it is related to the Vaccei, a well known Celtiberic nation (3) settled down on the central part on the North Meseta.

During the burial ritual (4), the corpse (fully dressed up) was burnt, and the resulting ashes kept in a vessel and buried. Therefore, some bronzes may show recrystalization structures due to the cremation, but most of the objects still kept their original metallographic structures.

METHODOLOGY

The metallographic preparation of ordinary bronzes is well known (5). But archaeological bronzes are actually very different: they should be regarded as a short of composite (an anhomogeneous mixture of different metals and oxidation products) so, when mounted in plastic material, a very slow six steps process has been found as the best: four grinding steps (grits 250, 500, 750 and 1000) and another two for polishing (with 7 µm and 3 µm diamond). But, as we were not allowed to cut or mount our specimens due to Spanish law restrictions dealing with archaeological finds, we were forced to hold the objects at necked hand while preparing their outer surfaces for examination. In this case, only two steps were followed: one for grinding (grit 500) and one for polishing (3 µm diamond). The result is a very bad picture with plenty of scratches and marks left by the polishing process, but which let us got, at least, an approach to the metal structure.

Alcoholic ferric chlorid was used a etching material ($\text{FeCl}_3+\text{C}_2\text{H}_5\text{O}+\text{HCL}$).
Objects were analyzed using XRF-EDS and ICP.

SUBJECT

Figure 1. PD/LR/II-C/76.

Figure 2. PD/LR/II-H/56.

Figure 3. PD/LR/II-AA/17.

Figure 4. PD/LR/II-AU/34.

Figure 5. PD/LR/IIAG/45.

Figure 6. PD/LR/III-E/51.

The six objects considered here are:

Figure 1. Arch. reference: PD/LR/II-C/76. Tower type fibula (400-350 BC). Composition: 95.24 %Cu, 1.86 %Pb, 2.51 %Sn.

Figure 2. Arch. reference: PD/LR/II-H/56. Top end of cross type fibula with double spring (400-300 BC). Composition: 93.12 %Cu, 0.98 %Pb, 5.07 %Sn.

Figure 3. Arch. reference: PD/LR/II-AA/17. Central part of horse type fibula (300-100 BC). Composition: 92.92 %Cu, 1.66 %Pb, 2.71 %Sn.

Figure 4. Arch. reference: PD/LR/II-AU/34. Ø type buckle (200-100 BC). Composition: 87.55 %Cu, 10.66 %Zn, 0.20 %Pb, 0.92 %Sn.

Figure 5. Arch. reference: PD/LR/IIAG/45. La Tène type fibula (100-50 BC). Composition: 80.06 %Cu, 11.92 %Pb, 7.07 %Sn.
Figure 6. Arch. reference: PD/LR/III-E/51. Hook from horse fitting (1000 BC). Composition: 86.88 %Cu, 2.07 %Pb, 4.75 %Sn.

EXPERIMENTAL

PD/LR/II-C/76, figure 7, shows the usual structures for 4th century BC objects: very small equiaxial grains with twin grains and, here, bending lines, all coming from a process of successive annealing and forging to form the object. Figure 8, top end of fibula, shows the same structure with greater damage from corrosion where stress from hammering was bigger, in the same way clearer shown in figure 9, a Danish head of a rivet from the Bronze Age. Figure 10, PD/LR/II-H/56, shows better recrystallization, as care had to be taken to forge the spring, so longer annealing times were used for this type. The very complicated in shape fibula PD/LR/II-AA/17, figure 11, is as cast, but shows many casting holes due to overheating of the bronze in the crucible. Later, all this problems disappear. PD/LR/II-AU/34, figure 12, is as cast, probably in hot mold or slightly annealed. PD/LR/II-AG/45, figure 13, very similar to the first object, was cast in a cold mold. PD/LR/III-B/51, figure 14, was cast and slightly annealed.

DISCUSSION

It has been shown that during a first period bronze work went from casting of simple figures which were later forged to get the final object towards bad casting of almost finished pieces. After this, together with the beginning of the Roman conquest, an improvement in casting techniques has been demonstrated.

This fits with other analytical results. Brass is only recorded after the 2nd century BC, together with a change in the copper smelting technology used for the copper imported by the Via de la Atalaya, as shown by the Fe and As content (7): iron increases with time, and arsenic has both very low or very high percentages till the 2nd century BC, which can be due to very low smelting technology, and later becomes homogeneous just below 1 %As, suggesting the generalization of the shaft furnace.

ACKNOWLEDGMENTS

We wish to thank the C.S.I.C. and the Fundación Caja Madrid for supporting the investigation leading to these results.

REFERENCES

2) Sanz, C., Uso del espacio en la necrópolis celtíbera de Las Ruedas, Padilla de Duero (Valladolid): cuatro tumbas para la definición de una estratigrafía horizontal, In (3): 371-396.
4) Sanz, C., Rituales funerarios en la necrópolis celtíbera de Las Ruedas, Padilla de Duero (Valladolid), in Burillo, F., Necrópolis Céltibéricas, 1990, Zaragoza, Fundación Fernando el Católico: 159-170.
Figure 7. PD/LR/II-C/76. 80x.

Figure 8. PD/LR/II-C/76. 80x.

Figure 9. Head of bronze rivet. 140x.

Figure 10. PD/LR/II-H/56. 100x.