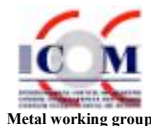


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METAL *Consn*-info



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Editorial

The last three months have been quite busy. Personally I moved again to a new country, Malta, which has joined the European Community recently. Malta is more known for its limestone used extensively in buildings than for its metal collections. Fortunately the knights of St John have left a very important collection of arms and armours exhibited in the Palace of the Grand Master in Valletta. The local atmosphere is very aggressive (high humidity, fluctuation of temperatures, marine salts) and for that reason local authorities have always tried to protect the collection. But all the protection systems tested up to now have failed. A new research has just started on the development of an innovative protection. It is presented in this issue.








Strangely most of the following abstracts are related to iron artefacts. It shows that research is still very active on this material especially on protection issues. To counterbalance these contributions, Blanca Rosales presents her research on outdoor bronze monuments in Buenos Aires.

BROME C has two new national correspondents: Alena Silhova representing Czech Republic and Prof Luiz Roberto Martins de Miranda representing Brazil. Thank you Alena and Luiz to accept this extra task.

Gerhard Eggert, German national correspondent of BROME C, had recently a brilliant idea about the future development of BROME C. Since it does not concern only the national correspondents but all the Metal WG members I decided to copy his message as it was sent to me: "Recently when I wanted to look up something in an earlier edition I had to browse through all issues which took considerable time. It is great to have BROME C on the web, but it is still the electronic counterpart of a printed newsletter. Why not publish it as a database with sections (past projects (with reference to literature, reports, a.s.o. if available), ongoing projects, future project plans) These sections could be subdivided into topics like metals in general, iron and steel (subsections: archaeology, craft objects, technical heritage), copper alloys... I think it would be much easier to find requested information". Gerhard mentioned to me that the extra work for that database should not be considerable since no new editorial work would be needed. It would consist in putting edited and reviewed information at the right place in such a software. Although I am totally for the idea, I just cannot do it. If one of the member is interested, he must contact me.

The Editor
Christian DEGRIGNY

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Ongoing research projects



Study of patinas formed on Cu base alloy monuments after outdoor exposure in Buenos Aires City (CITEFA)

The purpose of the study is the analysis of the protectiveness of natural patinas formed on monuments during long exposure periods. The main interest is to determine the best tailored intervention procedure for long lasting conservation.

This evaluation includes electrochemical characterisation of the corrosion products formed in very well defined laboratory conditions on Cu base statuary alloys with their analogous grown in the urban atmosphere of Buenos Aires city. Morphology is determined using scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX) to determine elemental composition and pollutant distribution. X-ray diffraction is applied for chemical composition characterisation.

In situ electrochemical potential measurements allowed a good correlation between both series of determinations on patinas of different protectiveness formed according to recipes of the artists. A set of statuary alloys with patinas formed according to original recipes applied before outdoor exposure of the work, and others modified to improve protectiveness, will be studied as formed and after different exposition periods to the atmosphere where most of our metallic sculptures have been installed. We are creating a catalogue of well characterised patinas to be applied to the restoration and conservation work. The characterisation involves the improvement of a quick electrochemical technique for evaluating "in situ" the protectiveness evolution with time.

M. A. Crespo, G. P. Cicileo, B. M. Rosales, "In situ" characterization of patinas formed on statuary alloys in laboratory and Buenos Aires city monuments", Proc. IV NACE Latinamerican Region and Latincor 2000, Cartagena de Indias, Colombia, 17 - 23 Set. 2000.

G. P., Cicileo, M. A. Crespo and B. M. Rosales, "Patina protectiveness evaluation of bronze monuments exposed to an urban atmosphere", Proc. 15th International Corrosion Congress, Paper 341, Granada, Spain, 22-27 Sept. 2002.

G. P., Cicileo, M. A. Crespo and B. M. Rosales, "Comparative study of patinas formed on statuary alloy by means of electrochemical and surface analysis techniques". Submitted for publication to Corrosion Science, Nov. 2002.

Contact: Blanca M. Rosales (CITEFA)

Funding: no external funding

Ongoing research project

Nickel enriched iron artefacts from Bohemia and Moravia (AIASCR)

Archaeological iron objects containing nickel and sometimes cobalt enriched structural phases have been of interest to many European archaeometallurgists for a long time. Some of the artefacts can reveal beautiful superficial pattern after surface polishing and etching due to the specific reaction of these phases. White lines are indeed formed which clearly indicate that the use of Ni-rich piled iron was intentional. However often Ni-rich lines are observed on the surface of common objects. In that case it is not clear yet whether the use of Ni-rich iron is accidental or not. Such objects seem to be quite rare. Among thousands and thousands of worldwide published metallographic examinations there are only several tens related to iron artefacts enriched sporadically by Ni. In the Czech Republic only one artefact (a 13th century axe) containing nickel was found before 2001, however since 13 other nickel-enriched iron objects have been identified: the 14th to 15th centuries iron fragment from Příšovice, the medieval spearhead from Turnov, the medieval or post medieval iron fitting from castle Trosky, the medieval horseshoe from Rovensko, the 13th century axe from Msténice, the 15th to 16th centuries fragment of a bit from Prague, the 9th to 11th centuries knife from Stara Boleslav, the 11th century knife from Budec, some 9th to 10th centuries artefacts as fragment of axe and gimlet from Pohansko, the gimlet from Nejdeč, two axes from Stare Město and from Ivanovice na Hane and finally the Celtic chisel from Stare Hradisko. In addition to these artefacts a piece of piled semi-product forged to make a knife was metallographically examined and streaks with nickel and cobalt were found. All the microanalyses were performed using EDX.

Up to now the following data have been obtained:

- 1) the nickel enriched phases have a typical appearance and can easily be recognised under metallographic examination and selected for further chemical analyses
- 2) the nickel rich bands in the same artefact vary in both the nickel and cobalt content, in hardness and also in thickness, therefore it is impossible to use them as provenance indicator (at least not at the scale of Czech Republic)
- 3) except perhaps for the 13th century axe it is not clear if the nickel-enriched iron has been intentionally used for the artefacts
- 4) traces of iron smelted from nickel-iron ores can be observed in all of the artefacts, however it seems that just the bit from Prague and the Celtic chisel from Stare Hradisko could have been entirely forged from a nickel enriched iron bloom.

In the future we would like to find out how many "nickel-enriched iron artefacts" actually exist in Bohemia and Moravia's collections. But first we have to re-equip our metallographic laboratory entirely destroyed during the last summer flood and to re-examine all of metallographic specimens stored in the Archaeological Institute of Prague (about 700 specimens). The second step will be to find out whether the nickel-enriched iron was used deliberately. Furthermore it would be interesting to search whether the nickel-rich iron ores are or not typical of Czech Republic (or more generally of Central Europe) than of other parts of Europe.

Contact: Jiri Hosek (AIASCR)

Fundings: no external funding

New research project

◆ New protection approaches for partly oxidised historic steel artefacts: Physical Vapour Deposition of inorganic and transparent films (MCR/DMME)

Historic iron based artefacts from public collections such as armours exposed to uncontrolled atmospheres (high humidity and fluctuating temperatures) are usually heavily corroded. Many different protections (varnishes, waxes and oils) have been tested in such corrosive environments but all of them failed up to now. The Armoury situated within the Palace of the Great Master of the Order of St John in Valletta is very representative of such endangered collections.

To improve the situation we have two options: to transform the environment in a safe one or to cover the artefacts with a more effective protection system. The exhibition halls of the Palace Armouries are suffering from rising damp. At times, and under certain atmospheric conditions, - these halls are transformed into “saunas”. It would cost a fortune to create a proper safe (stable) environment, and the only option we have is to define a new protection system which would resist such harsh conditions.

This conservation issue is the subject of a PhD research project conducted - at the Malta Centre for Restoration - MCR in collaboration with the Department of Metallurgy and Material Engineering - DMME (Faculty of Engineering) within the University of Malta. Due to new ethics in the field of armours conservation, protection systems will be applied on surfaces still covered with oxide layers supporting the original surface. The protection systems will have then to be effective on bare, partly oxidised or treated (gilded or painted) surface and respect certain criteria: reversibility (or at least retreatability), durability and minimum intervention. Traditional protection systems (varnishes, waxes...) will be tested as well as new transparent coatings obtained by Physical Vapour deposition (PVD) and developed at DMME.

In this latter technique, the coating material to be applied is targeted with a plasma electron beam causing its evaporation and eventual re-deposition onto the artefact under study. The whole process is carried out at fairly low temperatures and vacuum conditions. This treatment should allow the deposition process to occur with negligible alterations to the metal microstructure.

The research will start by a condition survey of the Palace Armoury in order to choose representative artefacts that will then be examined thoroughly. The second step will be the preparation of steel coupons simulating the behaviour of real artefacts. These will be used for the testing of the various protective systems available to date, as well as the newly developed PVD coating. A number of coupons will also be artificially corroded in a humid chamber and used to test the protection systems onto corroded surfaces. The third step will be the optimisation of the PVD coating. The final step will be to compare the effectiveness of this new protection system with - the traditional ones. The PVD coating is expected to perform much better than any as yet tested onto steel metal artefacts.

The choice of an appropriate steel for the preparation of our coupons is deemed - essential to this research project. We would therefore appreciate any information related to this matter from the WG members who have - expertise in the field of European armours dating from the end of the 16th century (or the start of the 17th).

Contact : Daniel Vella (MCR)

Funding: MCR / DMME

New research project

Development of protection systems for ethnographic iron artefacts (LAM / LCSM)

The objective of this project conducted at the Laboratory of Archeology of Metals (LAM) situated in Nancy by Nicolas Sanchez, student of a Master in Materials Science in collaboration with the Laboratory of Chemistry of Mineral Solid (LCSM), University Henri Poincaré, Nancy 1, is to determine the best protection system (varnishes, waxes...) on ethnographic iron artifacts.

It is divided in two steps. First artificial mild steel coupons will be prepared at the LAM. Surfaces will be micro-blasted, polished with micro-rotating tool and finally with paste. Afterwards they will be degreased with hydrosine and acetone. Different protection systems (acrylic varnish (Paraloid B72 et B88, 8% in acetone), microcristalline wax, « Balistol » oil, rust-convertoir Rustol, double layer acrylic varnish + microcristalline wax) will be applied by immersion or with a brush.

The coupons will be tested in a 3 electrodes electrochemical cell, the electrolyte used being distilled water to which Na_2SO_4 , NaHCO_3 and NaCl will be added. Coupons will be immersed during 21h before the start of the measurements.

Polarisation resistance (R_p) will be measured on a 2 hours period, every 15 minutes. Corrosion current (obtained with the Tafel method) will follow each R_p measurement (on a one hour period).

These tests should give us a rating of the systems tested.

The second step should confirm the preliminary rating. Coupons will be exposed to a humid chamber to simulate an accelerated ageing. The alteration will be assessed by the counting of pits formed on the surface of the coupons, the comparison of their weights before and after exposure and at the same time the observation of surface appearances on macroscopic photographs.

Contacts: Christine Riquier, Michel Folzan et Marie-Pierre Lambert (LAM)

Funding: no external funding

New research project

Conservation of burnt iron artefacts (*MATERIA VIVA/CIRIMAT/LIMAT/INPT*)

Iron artefacts represent a major part of archaeological remains recovered from excavations or from collections in storage. Their conservation is very challenging. Burnt iron artefacts, recovered from terrestrial sites (incineration burials, archaeological layers resulting from a fire) have developed a specific corrosion form and their behaviour during corrosion processes is quite untypical in comparison to the more traditional active corrosion. In addition these remains are difficult to identify. Classical cleaning and stabilisation procedures are usually applied to them. The increasing number of these excavated objects requires that a specific conservation protocol is defined for these objects, based on a better knowledge of the corrosion processes.

This project conducted in parallel to the research « Iron in ancient societies in Southern Regions» (France) is complementary to this one by its conservation approach. The study of burnt iron artefacts dating from the Iron Age I to Gallo-roman (625 B.C to the 3rd century A.C) has three objectives:

- the characterisation of corrosion layers and the establishment of their kinetic of formation
- the development of stabilisation protocols
- the establishment of an examination, conservation and preventive conservation strategy.

The studies are performed in collaboration with archaeologists and curators who were the first professionals in contact with the artefacts.

The partners of the project are MATERIA VIVA, the Research Unit 5085 -CIRIMAT (Centre Inter universitaire de Recherche et d'Ingénierie des Matériaux) Toulouse, the LIMAT (Laboratoire « Interfaces et Matériaux », Equipe de Recherche « Corrosion et Protection des Matériaux ») Toulouse, the National Polytechnics Institute of Toulouse and l'UMR 5608 - UTAH (Unité Toulousaine d'Archéologie et d'Histoire), University of Toulouse."

Contact: Monique Drieux Daguerre (MATERIA VIVA)

Funding: application for funds in progress

Calls for collaboration



Recent bibliography on conservation of aluminium alloys artefacts

Aluminium artefacts are typically found in ethnographic and industrial collections. Although there are many people working on them we do not find much publication on their conservation.

Some members from USA contacted me recently to have an up-dated bibliography on this topic. Although I worked in the field for some time, my subject was very limited since it concerned marine remains.

Any outcome from recent projects related to the examination, conservation or protection of these artefacts will be much appreciated.

Contact: Christian Degrigny

Calls for collaboration



Translation of Metal 2003 abstracts

Johanna Theile, conservator and lecturer at the Faculty of Art – University of Chile Las Encinas, Santiago de Chile has organised a seminar last April on the situation of metal conservation in Latin America (**1st Latino-American Congress on metal conservation** (7-11 April 2003, Museum of Contemporary Art, Santiago de Chile)). The seminar was held in Spanish but we would like to translate the abstracts both in English and French. Anyone who would volunteer for such a work would be more than welcomed.

Contact: Christian Degriigny

General information

- Future seminars and conferences
- The Group **Pre-industrial Metallurgical Arts and Techniques. Study and Conservation** organise a conference at the Musées Royaux d'Art et d'Histoire, Brussels : «*La sidérurgie avant le haut fourneau. Recherches sur les conditions techniques et historiques du développement de la sidérurgie en Lorraine avant la Guerre de Trente Ans*» on the 21 May 2003. For more information contact Monique de Ruelle (m.de.ruelle@kmg-mrah.be)
- **5th World Archaeological Congress (WAC5)** (21-26 June 2003, Catholic University of America, Washington, USA). For more information consult <http://www.american.edu/wac5>
- "**Preservation of Heritage Artifacts**" Conference (14-17 September 2003, Ottawa, Canada). Organised by the National Association of Corrosion Engineers (NACE) Northern Area Eastern. Deadline for abstracts is March 1, 2003 and for completed papers is June 1, 2003. For more information contact Lyndsie Selwyn, CCI, Ottawa (lyndsie_selwyn@pch.gc.ca)
- **Archaeometallurgy in Europe** (24-26 September 2003, Milan Italy). For more information consult <http://www.aimnet.it/archaeo.htm>

- Abbreviations and acronyms

AIASCR: Archaeological Institute of the Academy of Science of the Czech Republic (Prague)

CITEFA: Scientific and Technical Research Institute of the Armed Forces

DMME: Department of Metallurgy and Material Engineering

EDX: Energy Dispersive Spectroscopy

LAM : Laboratory of Archaeology of Metals

LCSM : Laboratory of Chemistry of Mineral Solid

MCR: Malta Centre for Restoration

PVD: Physical Vapour Deposition

SEM: Scanning Electron Microscope

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