Application of Thin Layer Activation in corrosion of bronzes

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Proton activation of a bronze alloy is investigated for the use of Thin Layer Activation (TLA) for surface degradation studies. For this purpose the reaction ^{65}Cu (p,n) ^{65}Zn is considered of interest. To obtain the optimum activation conditions and the calibration curve, relative γ-activity versus depth, various techniques were used. These included calculations of the yields using the computer code ALICE and experimental verification of the theoretical results by activation of bronze samples, using the stacked foil technique. These were used to determine the optimum activation conditions and to obtain the calibration curve. Activationof Cu based materials using protons of 11.5 MeV leads to a rather homogeneous distribution of ^{65}Zn over the first 130 μm, a very useful depth from an engineering point of view.

1 Introduction

Bronzes, alloys with as main constituents copper and tin, are used in a wide range of applications. They also form an important class of materials in cultural heritage. Depending on their use, they are prone to various surface degradation processes, such as wear and corrosion. Outdoor bronze statues for example are exposed to varying atmospheres causing corrosion. For studying these corrosion processes different techniques are used, including electrochemical, "spectroscopic", optical and surface analytical ones. Due to increasingly greater demands imposed on materials, advanced testing techniques are employed to establish their applicability. A very sensitive technique to measure material degradation from such processes as wear and corrosion, is that of Thin Layer Activation (TLA). The method comprises of generating at least one radionuclide in the material component by activation with charged particles and monitoring the loss of activity of the various radionuclides due to material loss [1,2]. To relate the technically relevant parameters in surface degradation, e.g. loss in material thickness, to the γ-activity, which is normally monitored, the relative distribution of γ-activity versus depth should be known. The largest use of TLA is in the field of wear testing of iron based materials, such as steels. Mostly activation of iron with protons is used and the relevant reactions are rather well known and were recently compiled [3]. There exists in the open literature a lack of data for the activation of various other elements.

2 Results and Discussion

In the present study proton activation of a bronze alloy is investigated preliminary to the use of TLA for surface degradation studies. For this purpose the reaction ^{65}Cu (p,n) ^{65}Zn is considered of interest, since ^{65}Zn has a half-life of 244 days, long enough to follow the phenomena for a technically relevant time.

Previous studies [4,5] indicated that there are several limitations and large levels of uncertainties in the prediction of absolute cross section data using computer codes. However, these codes provide useful representations of the shape of most excitation functions. Since the calibration curve needed in TLA studies is a representation of relative activity versus depth, it has been found that computer codes can be very useful for this purpose [6]. The results of the theoretical calculation with ALICE91 [7] of the cross section as a function of proton energy for the reactions ^{65}Cu (p,n) ^{65}Zn in pure natural Cu is shown in Fig. 1. The obtained data points were fitted with a polynomial function of the fourth degree. The maximum was estimated

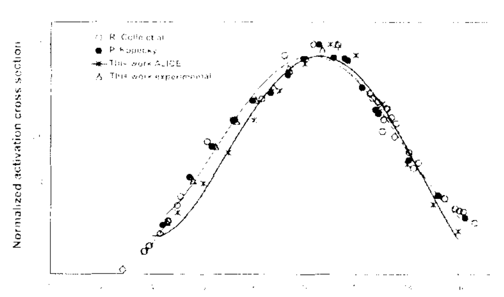

Figure 1 Normalized activation cross section as function of proton energy for the reaction $^{65}Cu_{29}(p,n)^{65}Zn_{30}$ calculated by ALICE and experimental values compared with literature data (R. Collé et. al. [8] and P. Kopecký [9]).

to be at 10.5 MeV for the reactions ^{65}Cu (p,n) ^{65}Zn. This is in good agreement with the literature [8-10]. The normalized cross section data of R. Collé et. al. [8] and P. Kopecký [9] fitted with a polynomial function of the fourth degree are also presented in Fig. 1. From these results the optimum energy for TLA application was chosen to be 11.5 MeV, corresponding to a theoretical yield of approximately 90% of the maximum value. This is expected to give a reasonable depth of activation as well as a rather homogeneous activation over a significant part of this depth. The latter condition makes quantification of material loss relatively easy, since it is directly related to activity loss.

Thick target yields for the proton induced production of ^{65}Zn as function of the energy, in the range of 11.5 to 4 MeV, have been measured experimentally via the stacked foil technique using a MC-40 variable energy cyclotron, having a 1% uncertainty in energy. Bronze foils of a composition Cu-5wt%Sn and a thickness of 25±1 μm were used for this purpose. A stack of 12 foils was irradiated with protons of 11.5 MeV. The ^{65}Zn activity induced in each foil was measured by γ-spectrometry system using a germanium detector. The γ-spectrometry system was calibrated both in energy and efficiency with standard emitting sources. The cooling time of the samples, approximately 7 days, and the measuring conditions were such that the interference free 1115 KeV γ-energy of ^{65}Zn could be measured with counting statistics better than 1%. Since for the purpose of the calibration curve only relative data is needed, no effort was made to obtain absolute data. The energy degradation of the proton beam through the foils was calculated from the energy projected range data output of the TRIM code [11]. The energy losses were 0.6 MeV in the first foil and 1 MeV in the last foil. The normalized data are also included in Fig. 1. The mean energy was taken as the proton energy at the middle of the foil. The experimental data are in good agreement with those of the literature.

The stacked foil data were used to obtain the calibration curve of ^{65}Zn for the condition of an 11.5 MeV incident proton beam. This curve is shown in Fig. 2 presented as relative activity, with the activity of the whole sample defined as 100%.

The data of Fig. 2 shows a deviation from the linear behaviour after 130 μm. Thus, a homogeneous distribution of ^{65}Zn is present in the first 130 μm, a very useful depth from an engineering point of view.

It can be concluded that although computer codes still possess significant limitations in the prediction of absolute cross section data, they are useful to assess the optimum experimental activation conditions for TLA studies.

TLA is a promising technique for bronzes corrosion studies.

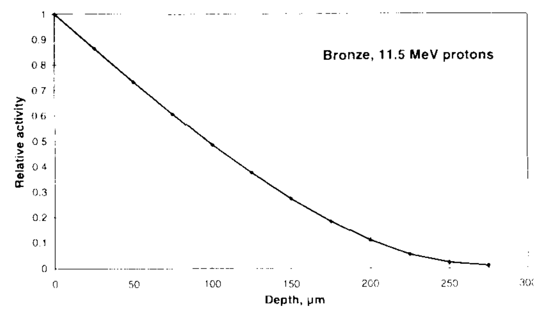

Figure 2 Relative ^{65}Zn activity versus depth for protons of 11.5 MeV in natural Cu-5wt%Sn measured experimentally using the stacked-foil technique.

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