



Nuclear Techniques in the Analyses of Magnesium-Based Alloys

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1. Introduction

The application of reliable techniques in the analyses of alloys used as biomaterials is of great importance because the element composition can influence their corrosion and consequently on the patient's health. The chosen implanted material should not cause adverse effects such as allergy, inflammation or toxicity either immediately after surgery or under post operative conditions [1]. Besides the presence of impurities in biomaterials, for instance, may initiate localized corrosion in relation to a grain causing early failure [2]. The use of magnesium and its alloys have been gaining great interest in medical devices which request biocompatibility and degradability [3-4]. However, its main limitation is the high corrosion rates, impairing the functioning of the material once they corrode before the cell healing [5]. Therefore, a chemical analysis is necessary to identify unwanted or unexpected impurities and whether the element concentrations are within their specification concentration ranges. In this way, biomaterial analysis is of interest not only for the health area but for the industries that produce them.

Several analytical techniques have been used for element determination in metallic alloys such as atomic absorption spectrometry (AAS), wavelength dispersive X-ray fluorescence spectrometry (WD XRFS), UV-vis spectrophotometry, inductively couple plasma by optical emission spectroscopy and atomic emission spectrometry (ICP-OES e ICP-AES), and neutron activation analysis (NAA) [6-11]. Among these techniques, NAA and WD XRFS were used in this study due to their advantages of the capability of a multi-element analysis for a wide range of mass fractions of elements without sample dissolution. The alloy dissolution is not always an easy task and also it requires the use of chemical reagents that can often contaminate the sample. WD XRFS is also considered an appropriate analytical tool for determining compositions due to a strong standardless quantification capability [12]. On the other hand, NAA allows to obtaining accurate results for majority and trace elements when compared with those obtained by AAS [13]. The objective of this study was to apply WD XRFS and NAA in the analyses of magnesium-based materials.

2. Methodology

The Mg based materials analyzed were commercially pure magnesium (CP-Mg) and AZ31 magnesium alloy. The CP-Mg was acquired in ingot form and the AZ31 Mg alloy was in sheet form of (30 x 30 x 1) cm. The preparation of these materials for NAA is described in the previous publication [14]. For WD XRFS analyses the alloy samples were cut using a mechanical guillotine in (15 x 15 x 1) mm dimensions. Then, these samples were cleaned under ultrasonic shaking for 15 min in each of the reagents: acetone PA, ethyl alcohol PA, and purified water. To obtain smooth and uniform surfaces, the samples were also sanded

using silicon carbide sandpaper successively with different grain sizes.

NAA analysis was carried out at the Neutron Activation Analysis Laboratory of the Research Reactor Center (CERPq) IPEN-CNEN/SP by irradiation at the IEA-R1 nuclear reactor. Synthetic element standards were irradiated with the samples for a short period (10 s under a thermal neutron flux of $1.9 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$) and long period (8 h under a thermal neutron flux of $4.5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$). About 50 mg of each sample were weighed in polyethylene envelopes for irradiation. After irradiation, the element standards and samples were measured using a Model GC 2018 Hyperpure Germanium detector coupled to a Digital Spectrum Analyzer (DAS 1000). The radionuclides measured were identified by their half-lives and gamma-ray energies. The element mass fractions were calculated using the comparative method [15]. The epithermal neutron activation analysis (ENAA) was carried out for Si determination by measuring ^{29}Al formed in the nuclear reaction $^{29}\text{Si}(\text{n,p})^{29}\text{Al}$. The ENAA procedure consisted of irradiating sample and Si standard of powder metallic silicon weighted in polyethylene involucres, for short irradiation of 60 s. The sample and Si standard were placed in a Cd capsule and irradiated under thermal and epithermal neutron flux of about $1.9 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ and $5.43 \times 10^{10} \text{ n cm}^{-2} \text{ s}^{-1}$, respectively. Results of quality control obtained in NAA are published in a previous publication [14]. WD XFRS analysis was carried out at the X-Ray Fluorescence Laboratory of the Chemistry and Environment Center (CEQMA) IPEN-CNEN/SP using the Model RIX 3000 X-ray spectrometer from Rigaku Co. The fundamental parameters method was applied for the quantitative determinations [16].

3. Results and Discussion

A great number of elements could be determined by NAA and WD XFRS in the magnesium-based materials. Table I shows the element mass fractions obtained in the commercial pure magnesium sample (CP-Mg) by NAA and these results presented good reproducibility for most of elements quantified. The exceptions were Fe, Sb and W. Silicon was not detected by ENAA, so detection limit value was calculated. The WD XFRS allowed the determination of Mg, Mn and S and this last element was not possible by NAA.

Table I: Element mass fractions in commercially pure magnesium sample (CP-Mg) by NAA and WD XFRS.

| Elements | N ^a | NAA | | WD XFRS M ± U ^d |
|------------------------|----------------|---------------------|----------------------|-------------------------------|
| | | M ± SD ^b | RSD ^c , % | |
| As, µg g ⁻¹ | 4 | 0.222 ± 0.017 | 7.8 | - |
| Cd, µg g ⁻¹ | 3 | 35.6 ± 2.4 | 6.6 | - |
| Co, µg g ⁻¹ | 4 | 16.1 ± 3.2 | 20.1 | - |
| Cr, mg g ⁻¹ | 3 | 4.90 ± 0.72 | 14.8 | - |
| Fe, mg g ⁻¹ | 4 | 3.09 ± 0.70 | 22.7 | <0.05 |
| In, µg g ⁻¹ | 3 | 106 ± 12 | 11.3 | - |
| La, µg g ⁻¹ | 4 | 0.344 ± 0.043 | 12.6 | - |
| Mg, % | 4 | 99.2 ± 2.7 | 2.8 | 99.9 ± 0.1 |
| Mn, µg g ⁻¹ | 5 | 698 ± 96 | 14.5 | 170 ± 20 |
| Mo, µg g ⁻¹ | 3 | 12.3 ± 1.1 | 9.2 | - |
| Na, mg g ⁻¹ | 4 | 0.498 ± 0.036 | 7.2 | - |
| S, % | - | - | - | 0.011 ± 0.001 |
| Sb, µg g ⁻¹ | 4 | 0.652 ± 0.187 | 28.7 | - |
| Si, % | 1 | <13.7 | - | - |
| V, µg g ⁻¹ | 3 | 8.79 ± 0.06 | 7.3 | - |
| W, µg g ⁻¹ | 3 | 45.0 ± 8.4 | 18.7 | - |
| Zn, mg g ⁻¹ | 3 | 0.104 ± 0.012 | 11.7 | <0.05 |

a. number of repetitions; b. arithmetic mean and standard deviation; c. relative standard deviation; d. mass fraction and expanded uncertainty calculated at 95 % of confidence level; -: not determined.

In the Table II, the mass fractions of 13 elements obtained in AZ31 magnesium alloy are presented. NAA results show good precision with relative standard deviations varying from 2.8 to 18.7 %. For Al, Cu, Mn and Zn, the results obtained are within the values presented in the specification document. Moreover, As, La, Na and Sb not presented in the specification, were quantified in this study and they could be considered as impurities. The element S and Ni could only be quantified in AZ31 alloy by WD XRFS.

Table II: Element mass fractions obtained in AZ31 alloy sample by NAA and WD XRFS.

| Elements | NAA | | WD XRFS | Reference [17] |
|--------------------------|-------------------|--------|-------------------|----------------|
| | M \pm SD | RSD, % | M \pm U | |
| Al, % | 3.06 \pm 0.19 | 6.1 | 2.7 \pm 0.1 | 2.5 – 3.5 |
| As, $\mu\text{g g}^{-1}$ | 2.30 \pm 0.34 | 14.8 | - | - |
| Cu, % | < 0.012 | - | - | <0.05 |
| Fe, % | < 0.095 | - | - | <0.005 |
| La, ng g^{-1} | 316 \pm 16 | 5.2 | - | - |
| Mg, % | 96.5 \pm 4.2 | 4.4 | 93.7 \pm 0.1 | Remainder |
| Mn, % | 0.325 \pm 0.013 | 3.9 | 1.0 \pm 0.1 | 0.2 – 1.0 |
| Ni, % | < 0.037 | - | 0.020 \pm 0.002 | <0.005 |
| Na, $\mu\text{g g}^{-1}$ | 397 \pm 32 | 8.1 | - | - |
| S, % | - | - | 0.06 \pm 0.01 | - |
| Sb, ng g^{-1} | 275 \pm 56 | 20.4 | - | - |
| Si, % | < 4.36 | - | - | <0.05 |
| Zn, % | 1.009 \pm 0.045 | 4.5 | 2.5 \pm 0.3 | 0.6 – 1.3 |

a. number of repetitions; b. arithmetic mean and standard deviation; c. relative standard deviation; d. mass fraction and expanded uncertainty calculated for 95 % of confidence level; -: not determined.

4. Conclusions

Nuclear techniques of NAA and WD XRFS applied in analyses of magnesium-based materials allowed the determination of several elements of the interest for the researches about its application as biomaterials. As conclusion, obtained results indicated the viability of using NAA and WD XRFS due to its multi elemental character in the determination of alloy main elements as well the impurities presented in low concentrations.

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