Determination of trace elements in metallic materials by neutron activation analysis

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Abstract. The aim of the present paper is to verify the applicability of neutron activation analysis to a metallurgic problem as a possible alternative technique to the standard investigation methodologies.

A first series of measurements was performed in order to check the feasibility of irradiation and counting over metallic samples. Some of the feared problems concerned an excessive activation of the matrix and the consequent difficulties in the spectrum interpretation, as well as the removal of the radioactive waste created by the irradiation.

Afterwards, a second series of measurements was performed to collect results aimed at the solution of a specific metallurgic case.

The tests were performed at the TRIGA MARK II reactor facility of the LENA (Laboratorio Energia Nucleare Applicata) Institute of the Pavia University.

1. Introduction

Metallic alloys usually can undergo different types of analyses, like chemical analyses - by wet method, quantometer, spectrometer - and analyses with RX fluorescence.

Moreover, other tests can be performed both in project and diagnostic phase: mechanical tests (e.g. tensile, hardness, hardenability, toughness), metallographic analyses, in the form of microographies for the interpretation of microstructures, the analysis of austenitic grain, the evaluation of non-metallic inclusions and macrographies, with the purpose to reconstruct the possible failure mechanism, and to gather information over samples of examined materials.

Finally, non-destructive tests can be performed by ultrasounds, penetrating liquids and radiographic systems.

However, when the quantities to determine are too small (order of magnitude: few ppm) or few technologies are currently available for the analysis of the desired elements, either because of the scarce industrial application of such elements, or because of objective difficulties in the development of the technology itself, other solutions must be found. The study of applicability of neutron activation analysis to the metallurgic field rises from these preliminary considerations.

2. Neutron activation analysis (NAA)

Neutron activation analysis consists in the creation of radioactive isotopes by neutron irradiation of the stable isotopes contained in an examined material and in the following analysis of the gamma decay affecting a number of them. As the emitted photons are characteristic
of the emitting nuclide, the gamma spectra collected after the detection process give useful
information about the chemical composition of the irradiated material, both from a qualitative
and quantitative point of view when co-irradiated with standards.

Neutron activation analysis is performed in three main steps: irradiation, detection and
interpretation of the results.

1. **irradiation** - In the irradiation process, the samples are immersed in a neutron field in
channels located within the core of a nuclear reactor. Some of the initial nuclides absorb
neutrons and transmute into unstable isotopes, thus undergoing one of the possible decay
branches. The capture cross section depends upon the target nucleus and the energy of
the incident neutron: in general, it increases with decreasing energies and this explains the
frequent choice of a mostly thermal \( E_n < 0.2 \text{ eV} \) irradiating beam;

2. **decay and detection** - Unstable isotopes decay in one of the possible disintegration
branches. In a number of cases the decay process leaves the daughter nuclide in an excited
state, from which it decays through the emission of electromagnetic radiation. The energy of
this radiation is characteristic of the nuclear structure of the emitting nuclide: the detection
of the emitted photons therefore leads to the identification of the emitting nuclide.

As photons do not carry electrical charge, the detection process is based upon indirect
methods, that is to say the collection of electron-hole pairs created by the interactions
between the ionising radiation and the matter in a semiconductor material (in our case,
High-Purity Germanium);

3. **data collection and interpretation of the results** - As a multi-channel analyser, a
software provides a representation of the collected information: in the present study,
GammaVision© 5.10 by EG&G ORTEC was used.

The collection of charged pairs created by the ionising radiation leads to a gamma spectrum
in which an energy interval is associated with a peak area representing the activity of a given
radioisotope.

Once individuated the energy interval corresponding to the emitted photon - and therefore
to the emitting nuclide - it is necessary to integrate the peak area and subtract the
background: the calculated area is proportional to the activity of the radioisotope. This is
the experimental information to insert in the computational procedures in order to obtain
the desired quantity.

In the measurement procedure it is commonly preferred to perform a differential measurement
of the activity rather than an absolute one. Indeed, the sample is irradiated simultaneously to
a reference standard material. Sample and standard spectra are then compared during the
computational phase, factorising away some systematic uncertainties - like those on counting
geometry and neutron flux - which otherwise may heavily affect the final results.

3. **Experimental campaign**

The LENA laboratory in Pavia is equipped with a research nuclear reactor TRIGA (Training
Research Isotope General Atomics) MARK II, designed for advanced neutronics and gamma-ray
studies, for radioactive isotope production and for sample activation (figure 1).

Activation analysis is there normally exploited in various applications, like environment and
organic material analyses, contamination measures, determination of age and geographic origins
of material samples. Yet, metallurgical investigations can not be considered, for the LENA
laboratory, as typical applications of this technique.

For this reason, in order to verify whether neutron activation analysis could be applied to this
special field, a case of rupture of a steel roll, cracked at the end of its heat treatment process,
has been studied.
The tempering steel-roll shown in figure 2 (a) had undergone a forging with long permanences at high temperature (700 - 1200 °C). It had then been normalized at a temperature below 900 °C and twice tempered at 400 and 250 °C, respectively. At the end of the heat treatment the roll had shown various superficially emerging cracks, which had ultimately made it unserviceable.

To try to reconstruct the failure mechanism, a number of samples were cut in different zones of the roll (figure 2 (b)) and mechanical tests were performed over them; they were then analysed with optical and scanning electron microscopy of the Università degli Studi di Brescia.

The information collected in such standard tests led to suppose that the intergranular cracks found in the roll had been caused by a grain-boundary embrittlement induced by the segregation of several trace elements [1]; it was also hypothesised that such segregation had occurred during the permanence of the roll at the high temperatures requested by the heat treatment, which is also responsible for an excessive growth of the austenitic grain and, consequently, for an intrinsic brittleness of the material.
Previous studies [2, 3, 4] indicated phosphorus, antimony and arsenic among the potentially
dangerous elements which may have segregated to grain boundaries in very small amounts, so
small that they could not be easily found through traditional methodologies.

Neutron activation analysis was therefore taken in consideration as a possible alternative
technique for trace element determination.

Two measurements were performed at an interval of few months one from the other.
The first one had the purpose to calibrate the methodology in its main parameters, like
irradiated quantities, irradiating times, time intervals between the end of irradiation and the
beginning of the counting, as well as the standards to co-irradiate with the samples. Some of
the feared problems concerned the detector masking due to an excessive activation of the iron
matrix, which may have caused problems in the removal of the radioactive waste, too.

Once verified the applicability of the method, another measurement was performed to focus
the attention on the specific metallurgic case, limiting the analysis to the investigation of few
elements in the most significant zones of the cracked roll.

3.1. The first measurement
For the first campaign, samples were cut both far and near the cracks of the roll. In order
to collect more information about the possible mechanism of failure, other two castings used
for the forging of two similar rolls, which had regularly been put in service, were taken into
consideration.

After their preparation, the samples were divided into three groups, which were irradiated
for a short, medium and long time, respectively, for the purpose of evaluating activities of
radionuclides characterised by different half-lives.

The standards used were powder multistandards previously certified by NIST: this choice rose
from the attempt to test the methodology for the recognition of as many elements as possible.

As an example, tables 1 and 2 show respectively the characteristics of the irradiations and
the results obtained from the analysis of medium half-life isotopes. The casting that gave origin
to the cracked roll has been labelled ‘A’, whereas ‘B’ and ‘C’ indicate the other two castings.

| Table 1. First irradiation - Analysis of medium half-life isotopes. The decay time represents the time between the end of the irradiation and the beginning of the counting. |
| Samples | Casting | Irradiation time [h] | Weight [mg] | Decay time [h] |
|---------|---------|----------------------|-------------|---------------|
| nm1     | A       | 1                    | 158.1       | 65.90         |
| nm2     | B       | 1                    | 118.2       | 71.92         |
| nm3     | C       | 1                    | 95.3        | 70.20         |
| Standards | Type | Irradiation time [h] | Weight [mg] | Decay time [h] |
| sm1     | 1633a   | 1                    | 161.3       | 68.18         |
| sm2     | 1632a   | 1                    | 64.9        | 69.35         |
| sm3     | 1632a   | 1                    | 114.8       | 72.7          |
| sm4     | 1633a   | 1                    | 175.5       | 74.48         |

The global results showed a good sensitivity of the method to many of the investigated
elements; particularly significant were the results obtained for As and Sb, whose peaks in the
spectra looked sharp and definite.
Table 2. First measurement - Analysis of medium half-life isotopes.

| Element | Chemical analysis [ppm] | Isotope | Peak energy [keV] | sm1 [ppm] | sm2 [ppm] | sm3 [ppm] | sm4 [ppm] |
|---------|-------------------------|---------|-------------------|-----------|-----------|-----------|-----------|
| A       |                        |         |                   |           |           |           |           |
| As      | 70                      | 76As    | 559.1             | 67.96     | 74.84     | 68.69     | 69.55     |
| Sb      | 10                      | 122Sb   | 564.1             | 16.35     | 15.48     | 17.87     | 17.41     |
| Co      | 120                     | 60Co    | 1173.2            | 113.58    | -         | -         | 132.84    |
| B       |                        |         |                   |           |           |           |           |
| As      | -                       | 76As    | 559.1             | 51.77     | 57.01     | 52.32     | 52.98     |
| Sb      | -                       | 122Sb   | 564.1             | 12.77     | 12.09     | 13.95     | 13.59     |
| Co      | -                       | 60Co    | 1173.2            | 93.26     | -         | -         | 109.06    |
| C       |                        |         |                   |           |           |           |           |
| As      | 70                      | 76As    | 559.1             | 61.92     | 68.19     | 62.58     | 63.37     |
| Sb      | 9                       | 122Sb   | 564.1             | 15.48     | 14.65     | 16.92     | 16.48     |
| Co      | 100                     | 60Co    | 1173.2            | 118.20    | -         | -         | 138.24    |

3.2. The second measurement

Once verified that activation analysis could be applied successfully to metallurgic investigations, a second series of measurements was planned to search only for the potentially dangerous trace elements in one of the crack zones.

Three different samples were cut right below the surface, to avoid the strongly oxidised superficial layer created during the high-temperature heat treatment.

In this case, the standard used was a coal fly ash multistandard, also certified by NIST.

The analysis was restricted to As and Sb, whose unstable isotopes $^{76}$As and $^{122}$Sb have medium half-lives. In table 3 the general pieces of information about the second campaign are shown.

Figure 3 shows an example of the spectra obtained for the samples and the co-irradiated standards.

The data collected from this second measurement and reported in table 4 confirmed the results of the first one, in substantial agreement with the average data of the chemical analyses provided by the steelworks.

In all the samples, the anomalies - in terms of increased amounts of trace elements - which had been expected in the preliminary phase have not been observed (with the exception of a slight increase in arsenic amount noted in the second series of measurements, performed right below the fracture surface).

This does suggest that other elements (possibly phosphorus [5, 6, 7]) may have been the principal responsible for the integranular cracks.
Table 3. Second irradiation - Analysis of $^{76}$As and $^{122}$Sb.

| Samples | Casting | Irradiation time [h] | Weight [mg] | Decay time [h] |
|---------|---------|----------------------|-------------|---------------|
| m1      | A       | 2                    | 294.5       | 22.30         |
| m2      | A       | 2                    | 334.5       | 23.82         |
| m3      | A       | 2                    | 428.5       | 21.70         |

| Standards | Type | Irradiation time [h] | Weight [mg] | Decay time [h] |
|-----------|------|----------------------|-------------|---------------|
| s1        | 1633a| 2                    | 228.8       | 24.68         |
| s2        | 1633a| 2                    | 267.3       | 22.77         |
| s3        | 1633a| 2                    | 252.7       | 24.37         |

Figure 3. Spectrum from the counting of m1 sample.

4. Accuracy of the method
The expression of the mass of the trace element to be determined $m$ is given by:

$$m = \frac{n^{riv}_\gamma (\Delta \tau) A \lambda}{\sigma \Phi N_0 \theta \mathcal{F} \eta \cdot (1 - e^{-\lambda t_i}) \cdot e^{-\lambda \tau_a} \cdot (1 - e^{-\lambda \Delta \tau})}$$  \hspace{1cm} (1)

where $n^{riv}_\gamma$, $A$, $N_0$, $t_i$, $\tau_a$ represent the number of photons detected in a time interval $\Delta \tau$, the atomic mass, Avogadro number, the irradiation time and the decay time, respectively. This expression shows that the measurement is affected by various uncertainties: the capture cross section $\sigma$, the isotopic abundance $\theta$, the decay constant $\lambda$, the photonic emission probability $\mathcal{F}$. Moreover, indeterminations on geometrical and instrumental factors must be considered: the neutron flux $\Phi$, the solid angle between the detector and the gamma emitter $\Omega$, and the detector efficiency $\eta$.

In the present campaign, thanks to the choice of a differential measurement and the use of reference standard materials, the unknown quantity is evaluated by comparison:

$$m = m_0 \cdot \frac{n^{riv}_\gamma (\Delta \tau) \cdot (1 - e^{-\lambda t_i}) \cdot e^{-\lambda \tau_a} \cdot (1 - e^{-\lambda \Delta \tau})}{n^{riv}_\gamma (\Delta \tau_0) \cdot (1 - e^{-\lambda t_0}) \cdot e^{-\lambda \tau_0} \cdot (1 - e^{-\lambda \Delta \tau_0})}$$  \hspace{1cm} (2)
### Table 4. Second measurement - Results for $^{76}$As and $^{122}$Sb analysis [%].

|     | std. ⇒ | s1  | s2  | s3  | avg. | std. dev. |
|-----|--------|-----|-----|-----|------|----------|
| As  | smp. ↓ |     |     |     |      |          |
| m1  | 0.0086 | 0.0080 | 0.0087 | 0.0084 | 0.00036 |
| m2  | 0.0067 | 0.0063 | 0.0068 | 0.0066 | 0.00028 |
| m3  | 0.0074 | 0.0070 | 0.0076 | 0.0073 | 0.00031 |

|     | std. ⇒ | s1  | s2  | s3  | avg. | std. dev. |
|-----|--------|-----|-----|-----|------|----------|
| Sb  | smp. ↓ |     |     |     |      |          |
| m1  | 0.0011 | 0.0012 | 0.0012 | 0.0011 | 5.11 · 10$^{-5}$ |
| m2  | 0.0009 | 0.0010 | 0.0010 | 0.0009 | 4.19 · 10$^{-5}$ |
| m3  | 0.0010 | 0.0010 | 0.0012 | 0.0010 | 4.57 · 10$^{-5}$ |

where subscript '0' indicates quantities with reference to the standard.

As the sample and the standard have been irradiated simultaneously and for the same
irradiating and counting time ($t_i = t_{0i}$ and $\Delta \tau = \Delta \tau_0$), Eq. (2) becomes

\[ m = m_0 \cdot \frac{n_{riv,0}^{\gamma} (\Delta \tau) e^{-\lambda \tau_0}}{n_{riv,0}^{\gamma} (\Delta \tau) e^{-\lambda \tau_0} + n_{riv}^{\gamma} (\Delta \tau) e^{-\lambda \tau_0}}. \]

Considering that time uncertainties (both relatively to the decay time and the counting time)
can be neglected, the overall mass indetermination can be found as

\[
\frac{\sigma(m)}{m} = \sqrt{\frac{\sigma^2(m_0)}{(m_0)^2} + \frac{\sigma^2(n_{riv}^{\gamma})}{(n_{riv}^{\gamma})^2} + \frac{\sigma^2(n_{riv,0}^{\gamma})}{(n_{riv,0}^{\gamma})^2}} = \sqrt{\frac{\sigma^2(m_0)}{(m_0)^2} + \frac{1}{n_{riv}^{\gamma}} + \frac{1}{n_{riv,0}^{\gamma}}},
\]

where $m_0$ is known with very high precision and $\frac{\sigma(m_0)}{m_0}$ is negligible.

Moreover, as the standards used contain much more of the analysed substance in comparison
with the samples, the standard’s activity after the irradiation is quite higher than the sample
one, so that $n_{riv,0}^{\gamma} \gg n_{riv}^{\gamma}$.

Therefore, with respect to the operating conditions adopted in the present measurements, the
simplified expression of the mass uncertainty is

\[
\frac{\sigma(m)}{m} = \frac{1}{\sqrt{n_{riv}^{\gamma}}}. \]

According to this approximation, a 3%-mass indetermination can be obtained with $n_{riv}^{\gamma} \approx 10^3$, that is to say with the collection
of more than one thousand counts from the detection process.

It is nevertheless opportune to underline that in general other factors may influence the
minimum number of counts which is necessary to get an acceptable result (e.g. the entity of the background).

### 5. Conclusions and prospects

Neutron activation analysis proved to be applicable to typical metallurgic problems in spite
of possible excessive activation of the matrix and consequent difficulties in the measurement
procedure and removal of radioactive waste.
Considering the obtained results and the tolerable costs of the measurement procedure, we can conclude that neutron activation analysis is proposable for metallurgical analysis beside the standard methodologies applied in such field.

The use of neutron activation analysis technique for metallurgic aims shows various advantages in comparison with traditional methodologies:

- higher sensitivity
- possibility to evaluate simultaneously many elements (thanks to the spectrum display)
- versatility (for the possibility to adjust the different parameters accordingly to each purpose)
- high applicability.

As the procedure can be applied to steel samples, it is possible to use it also in problems concerning other ferrous alloys, like cast irons. These materials are wholly analogous to steels from an irradiation point of view, as the difference between them simply lies in the different percentage of carbon in their composition.

In particular, ductile cast irons can be investigated through neutron activation analysis because of the peculiar technology involved in their production.

Ductile irons possess reasonably high strength, good ductility and resistance to shock. Ductile cast irons also have some attractive properties, such as castability, machinability, wear resistance and impact resistance, as compared to those of steel [8]. As a result, they have been used in many industrial sectors. The graphite contained in a ductile cast iron is characterised by a round shape, which contributes enhancing the macroscopic mechanical properties of the material and makes it attractive in many industrial sectors. This shape is obtained by addings of various elements, like rare earths, in small and precise amounts.

As neutron activation analysis has proved to be very sensitive to the detection of such elements even in such small amounts, it is proposable for the inspection and the control of these critical compositions.

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