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Oxygen Determination in Aluminium Iron Pre-Alloyed Powders by Nuclear Reaction Analysis

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Résumé. — L'oxygène contenu dans des alliages Al-3%Fe ou Al-8%Fe-1%Zr (% massique) fabriqués par atomisation dans l'air de poudres qui ont été ensuite frittées puis forgées dans une gamme de température comprise entre 320 et 500 °C, a été déterminée par réactions nucléaires (N.R.A.). Les résultats, obtenus avec une incertitude estimée $\pm 15\%$, révèlent un taux d'oxygène de 1 à 2% en masse. Ces poudres ont en fait adsorbé une assez grande quantité d'eau et d'oxygène pendant le processus d'atomisation dans l'air ou au cours de leur stockage, conduisant à la formation d'oxydes et hydroxydes métalliques. Après traitement thermique des échantillons au-dessus de 200 °C, seul l'alumine reste présent, ce qui explique les différences constatées entre les teneurs en oxygène des échantillons comprimés à température ambiante et ceux forgés à chaud.

Abstract. — Oxygen content in aluminium alloys Al-3Fe or Al-8Fe-1Zr (wt%) made from air atomized powders by a sinter-forging process (in the range of 320 to 500 °C) has been determined by using a Nuclear Reaction Analysis (N.R.A). The amount of Oxygen, either in pressed compacts or in hot-forged samples was measured with an accuracy of $\pm 15\%$ and found to be equal to 1-2 wt%. In fact, during atomization in air and/or their subsequent storage, these powders have adsorbed a rather important quantity of oxygen and water vapor leading to the formation of oxides and hydroxides. Only after outgassing over 200 °C, Al_2O_3 is kept, which explains differences in oxygen content in pressed or hot forged samples.

1. Introduction

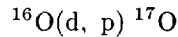
Aluminium alloys are widely used in different fields such as road or air transport, packaging, car and shipping applications. In particular, the structural hardening aluminium alloys of series 2000, 6000 and 7000, have good mechanical characteristics and are corrosion resistant; moreover, they have a rather low density, and may be easily shaped. Nevertheless, these materials cannot be used for parts working at temperature higher than 150 °C: over this temperature, hardening precipitate phases coalesce, which induces an irreversible decrease in mechanical properties.

New aluminium alloys keeping a high yield-stress up to 300 °C may be manufactured by adding elements such as Fe, Cr..., with a very low solubility in the solid state, able to form intermetallic compounds [1]. The specific effect of a Zr addition is to reduce the mean grain size and delay the coarsening of Al₃Fe₄ precipitates.

These materials are manufactured from rapidly solidified powders using forging and/or extrusion processes. During atomization, an oxygen surface contamination occurs which can be exaggerated during storage; these oxide layers may affect badly the sintering process or reduce the mechanical properties because oxides are located at grain boundaries. Thus, the measurement of oxygen contamination is desirable which can be made by Nuclear Reaction Analysis as shown in this study.

1.1. NUCLEAR REACTION. — The Nuclear Reaction Analysis (N.R.A) is a technique which consists in detecting the particles or photons emitted by a material, when bombarded with a high energy charged particle beam. Contrary to ESCA, it does not provide information about the chemical bonds, but on the presence of low atomic mass nuclei and their distribution inside the material.

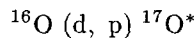
When bombarding a material, the energetic charged particles (in the range of 1 MeV) penetrate the matter, slow down (due to electronic interactions), and finally stop at some ten micrometers depth under to irradiated surface of the sample. In the range of few micrometers depth, nuclear reactions may occur. For oxygen, the nuclear reaction of interest is:



where:

- ¹⁶O is the target nucleus and ¹⁷O the residual nucleus,
- d is the incident deuteron and p the emitted proton.

In such a reaction, the ¹⁷O nucleus is produced in a highly excited state. The corresponding proton kinetic energy depends on the impinging deuteron energy and the angle between the impinging deuteron direction and the emitted proton direction [2, 3]. It can be calculated by applying the energy and impulsion conservation laws. For oxygen, the probability that the residual nucleus will be excited is high. So, in order the oxygen analysis to be performed, the reaction used is actually:



where ¹⁷O* is the first excited level nucleus and p the corresponding emitted proton. However, several other light elements, like carbon and nitrogen, may be present inside the material analyzed and several nuclear reactions may occur. Furthermore, penetrating inside the material, the deuterons are slowed down, and deeper the reaction lower the emitted proton energy. In order to distinguish the emitted protons of interest from others, a spectrometry of the detected charged particles was performed.

In the other hand, the nuclear reaction probability varies as a function of the incident particle energy. A differential cross section $\frac{d\sigma}{d\Omega}$ is then defined, for a given detection angle and a given impinging energy.

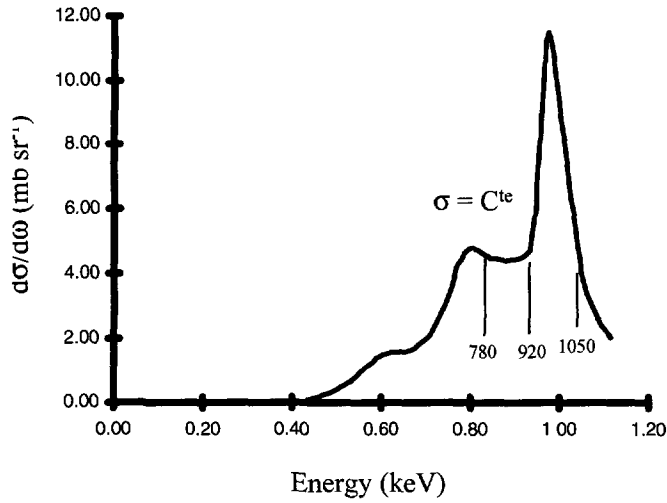


Fig. 1. — The differential cross section of the reaction [4].

For a homogeneous sample, nuclear reaction quantitative analysis may be performed if the following equation is solved:

$$N_p = N N_d \Delta\Omega \frac{1}{\Delta X} \int_X^{X+\Delta X} \left(\frac{d\sigma}{d\Omega} \right)_{\theta, E(x)} dX \tag{1}$$

where:

- N_p is the number of detected protons emitted from a slice of thickness Δx , in the $\Delta\Omega$ solid angle,
- N , the number of oxygen nuclei inside the analyzed material,
- N_d , the number of impinging deuterons,
- $\left(\frac{d\sigma}{d\Omega} \right)_{\theta, E(x)}$, the differential cross section for θ angle for energy E , at depth x ,
- θ , the detection angle.

For solving the above integral, the mathematical form of the cross section variation as a function of the energy must be known. There are two situations for which equation (1) can easily be solved:

- i) the sample is thin, i.e. the deuteron energy loss inside the material is low, then the cross section variation along the deuteron trajectory is negligible.
- ii) the sample is thick and the energy loss charged particles inside the target is not negligible, but the cross section keeps a constant value over an energy range of known magnitude.

The excitation curve of the reaction, published by Amsel *et al.* [4] (Fig. 1), shows that the differential cross section is almost constant between 780 and 920 keV. Within this energy range, equation (1) can be applied, where $\frac{d\sigma}{d\Omega}$ has a fixed value. This condition may be kept for nuclear reactions occurring inside a material slice in which the deuteron energy range is between these two values.

Equation (1) is then simplified and the quantitative analysis performed by using the following expression:

$$N_p = N N_d \frac{d\sigma}{d\Omega} \Delta\Omega \frac{1}{\Delta X} \int_x^{x+\Delta X} dX \quad (2)$$

The cross section $\frac{d\sigma}{d\Omega}$ is given in cm^2 (1 barn = 10^{-24} cm^2) and N is the number of oxygen atoms in the corresponding slice (at cm^{-2}).

In order to determine the oxygen concentration, it is then necessary to establish the correspondence between the analyzed slice thickness and the region of interest in the experimental spectrum. This is made by calculating the so - called "depth-energy correspondence".

1.2. DEPTH-ENERGY CORRESPONDENCE (FIG. 2). — When penetrating inside a material, the energy loss of a particle depends on the "stopping power" of the material. This important parameter depends on the material composition and on the nature (deuteron, proton,...) and energy of the particle. For a given material and a given particle, a differential stopping power S is then defined:

$$S = -\frac{dE}{dx}$$

Bombarding the surface of a sample with particles of impinging energy E_d , the particle energy $E(x)$ at the depth x under the irradiated surface is equal to:

$$E(x) = E_d - \int_0^x S dx \quad (3)$$

Conversely, the thickness Δx of a given material slice (Fig. 2a), necessary to obtain a particle slowing down $\Delta E = E_d - E(x)$, can be calculated by solving the following equation:

$$\Delta x = - \int_{E(x)}^{E_d} \frac{1}{S} dE \quad (4)$$

Calculating the emitted proton energy for impinging deuterons of respectively 920 and 780 keV, and solving equations (3) or (4) for the impinging deuterons and emitted protons, it is possible to define an energy range (a "window ") in the detected proton energy spectrum, corresponding to an analyzed slice of thickness Δx , inside the material (Fig. 2b).

To solve these equations, a computer program (PYROLE code) [5] has been developed by Ph. Trouslard; the stopping power is calculated with the procedure of Andersen and Ziegler [6] and the additivity law in the case of a multi-elementary component. In order the analyzed slice thickness to be determined, the sample is divided into homogeneous thin layers. Inside each layer, the energy loss is fixed (typically 3 keV), and the stopping power maintained at a constant value. An iterative process is then performed.

2. Analysis Procedure

To eliminate experimental errors, a comparative quantitative analysis method has been carried out: the number N_p of protons emitted from the analyzed sample is measured and compared with the number N_{p_0} of protons emitted from a standard thin sample (using a thin sample, instead of thick sample, to avoid errors on the evaluation of the standard analyzed slice thickness).

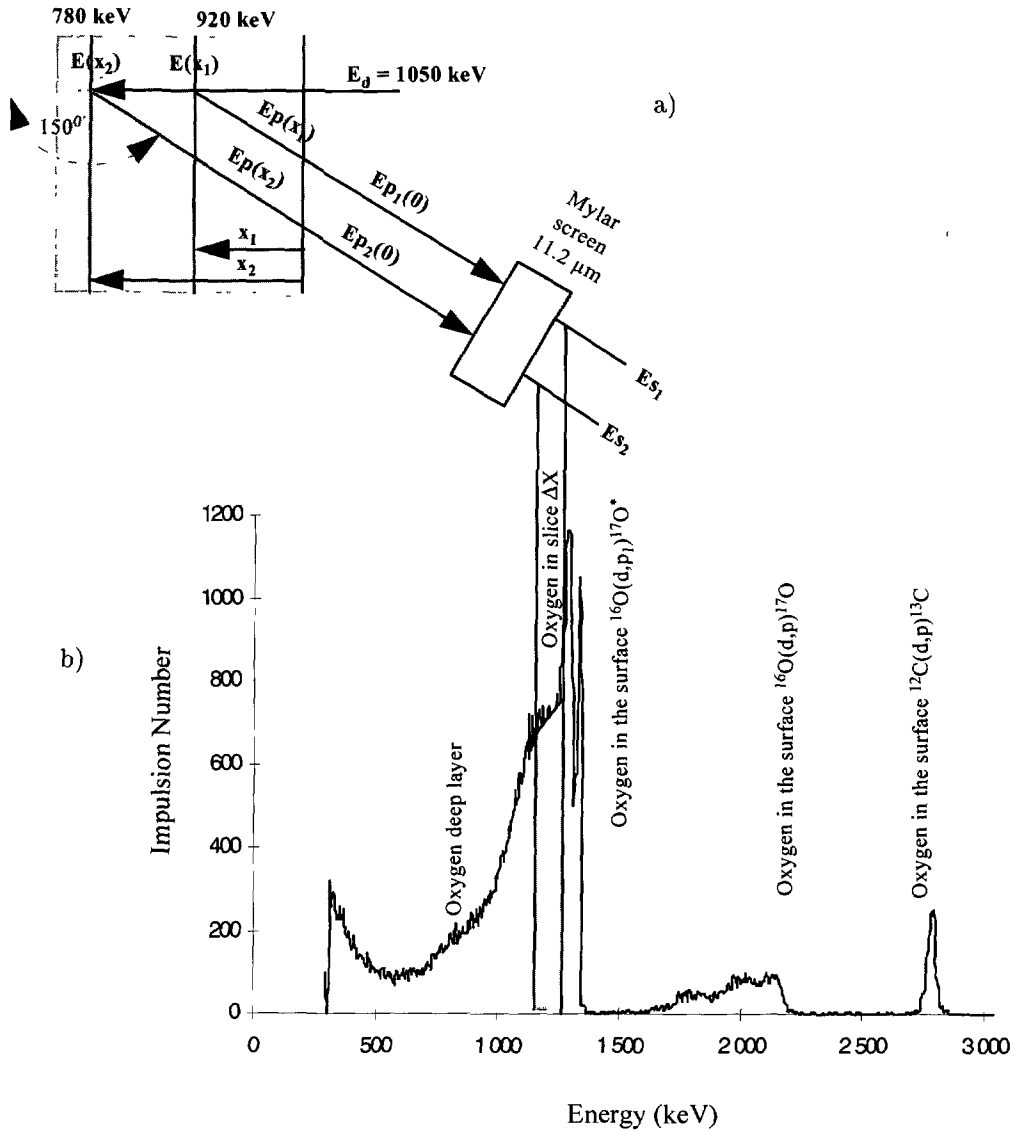


Fig. 2. — Depth - energy correspondence.

The total number of impinging deuterons N_d is deduced from the integrated electric charge Q (measured directly on the sample) by:

$$N_d = \frac{Q}{e^-} \tag{5}$$

where e^- is the electrical elementary charge (1.6×10^{-19} C).

Applying equations (2) and (5) for both unknown and reference samples and making the ratio between the two expressions, it comes:

$$N = N_0 \frac{N_p}{N_{p0}} \frac{Q_0}{Q} \quad (6)$$

where:

- N_0 is the number of oxygen atoms in the standard sample (at cm^{-2}),
- Q and Q_0 the integrated charge, measured on the sample and the standard respectively.

The oxygen concentration (in weight percent) is finally given by the following expression, directly deduced from equation (6):

$$T(\%) = \frac{M}{\mathcal{N}} N_0 \frac{N_p}{N_{p0}} \frac{Q_0}{Q} \frac{1}{\rho \Delta x} 100 \quad (7)$$

where:

- M is the atomic mass of oxygen (g),
- \mathcal{N} , the Avogadro number,
- ρ , the sample density (g cm^{-3}),
- Δx , the thickness of the analyzed sample slice (cm).

3. Experimental

3.1. SAMPLE PREPARATION. — Pre-alloyed powders of different granulometry (in the range of 40 to 400 micrometers) prepared by atomization have been selected. Two series of samples have been then prepared:

- both Al-3Fe and Al-8Fe-1Zr (wt%) powders were pressed at room temperature, in order to obtain small pressed compacts ($19.5 \times 4 \times 2$) mm^3 .
- Some of the above pellets of each category were sinter-forged at different temperatures (in the range of 320 to 500 °C).

The samples were then mechanically polished.

3.2. EXPERIMENTAL EQUIPMENT AND SET-UP. — The nuclear reactions were performed with a deuteron beam of 1 mm in diameter and 100 nA in intensity, delivered by the 2.5 MV Van de Graaff accelerator of INSTN - Saclay.

The samples were placed under vacuum (2×10^{-6} Torr) on a sample holder connected to an ORTEC digital current integrator for measuring Q values. The emitted protons were detected at $\theta = 150^\circ$ with an ORTEC semiconductor, behind a 11 micrometers mylar screen (in order to eliminate the scattered deuterons).

The proton energy spectra were recorded with a Canberra multi-channel analyzer and stored with a compatible PC computer.

3.3. ANALYSIS PROCESS. — The thickness of analyzed material slices, in which the entering deuteron energy was 920 keV and the coming out energy 780 keV, has been calculated with the PYROLE code. Increasing the impinging energy, the analyzed slice is "shifted" inside the sample, at the corresponding depth, so that it becomes possible to determine the depth profile of oxygen distribution inside the sample.

More simply, choosing a precise incident beam energy, we determine one analyzed slice, at a given depth below the surface.

As a reference, a thin film of tantalum oxide [7] (Ta_2O_5 : $352 \times 10^{15} \pm 3\%$ atoms of oxygen per cm^2) was bombarded with a 920 keV deuteron beam.

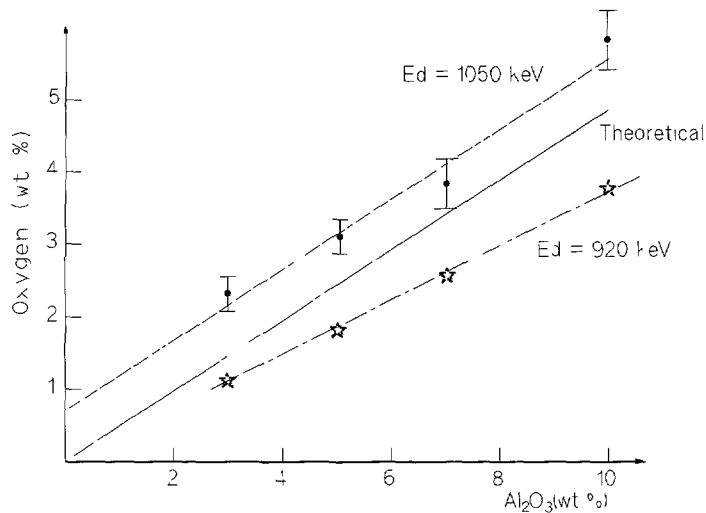


Fig. 3. — Variation of oxygen content as a function of Al₂O₃ addition.

4. Testing

Three successive adjacent layers of equal thickness have been defined (in the range of 1.72 to 2.04 micrometers, according to the different analyzed material composition and density). The corresponding incident beam energies, calculated with the PYROLE code, were respectively: 920, 1050 and 1170 keV.

We observed that the first layer composition is quite inhomogeneous (due to the sample preparation and storage in air). Furthermore, we observed that the deepest layer is not easy to investigate, because the corresponding proton energy range is low and located in a spectrum region where the electronic background is high. Finally, the second slice under the surface has been analyzed, as characteristic of the bulk composition of the material (Fig. 2b).

In order to confirm the efficiency of the method, preliminary testing was carried out on a series of reference pressed samples (aluminium powder mixed with alumina powder, in known proportions, then compacted).

The calculated oxygen contents and the experimental results are compared in Figure 3, and confirm the inhomogeneity of the superficial layers.

In the other hand, the results obtained by analyzing the second slice show that the proportionality between the alumina addition and the corresponding oxygen concentration is verified by the analysis process. We also see that the results are higher than expected (about 0.8%), certainly due to a previous oxidation of the aluminium powder. To confirm this point, a plate of pure aluminium was analyzed: only traces of oxygen were effectively found in the bulk material (about 530 ppm in mass).

5. Results and Discussion

The results for the different samples are reported in Table I for Al-3%Fe and Table II for Al-8%Fe-1%Zr alloys.

- For Al-3%Fe, we found that, before forging, materials elaborated from the finest powder (25-50 μm) have a higher oxygen concentration (more than 2.5%).

The oxygen concentration is slightly lower in the other cases (in the range of 1.76 to 2.02%).

Table I. — *Oxygen concentration for the samples Al-3%Fe.*

Material Al-Fe	Density	Depth (μm)	Oxygen (wt%)	Uncertainty on Oxygen content (%)
Powder pressed before sieving	2.63	1.93	1.83	± 15.3
(25-50 μm)			2.53	± 15.6
(50-100 μm)			1.80	± 15.3
(100-160 μm)			1.87	
(160-200 μm)			2.02	
(200-315 μm)			1.76	
(315-400 μm)			1.83	
After sinter-forging at 370°C	2.76	1.84	1.16	
After sinter-forging at 420°C	2.77	1.83	1.17	± 15
After sinter-forging at 500°C			1.20	

- For Al-8%Fe-1%Zr, the oxygen concentration is lower.

After forging, the oxygen concentration is clearly lowered (1.16 to 1.20%), and the forging temperature has no influence. We can conclude that all hydroxides are eliminated below 370 °C. This was confirmed by Infra Red Spectrometry which shows that, above 350 °C, there is no more oxygen release. Above this temperature, only alumina is stable inside the material.

We can suppose that alumina was formed during the atomization process, so that each pre-alloyed particle is covered with a thin alumina layer. Using a simple model to describe the forged or compacted material structure (pure aluminium jointed cubes of the same size than the grain one, each grain being covered with an alumina layer of thickness X), one can easily find that such an amount of oxygen would represent layers of about 400 nm in thickness, which is much more (about 10 or 20 times) than the natural surface film covering an aluminium plate, stored in air [1]. This model is not sufficient to describing correctly the oxygen distribution inside the sample.

The global uncertainty on the results is obtained from equation (7) using the errors propagation method [8,9] and is found $\pm 15\%$. The main contributions to the total uncertainty concern the following parameters: the number of oxygen atoms in the standard (3%), the spectrum peak surface (1.5%), the beam current measurement (3%), the sample density (2%) and the thickness of the corresponding analyzed slice (10%).

Table II. — *Oxygen concentration for the samples Al-8%Fe -1%Zr.*

Material Al-Fe-Zr	Density	Depth (μm)	Oxygen (wt%)	Uncertainty on Oxygen content (%)
Powder pressed before sieving	2.52	2.04	1.90	± 15.3
(50-100 μm)			1.50	± 15.5
(100-160 μm)			1.32	
(160-200 μm)			1.26	
After sinter-forging at 350°C	2.81	1.83	1.11	± 15.6
After sinter-forging at 400°C	2.87	1.79	1.16	
After sinter-forging at 500°C	2.98	1.72	1.15	

Conclusion

Aluminium alloys Al-3%Fe and Al-8%Fe-1%Zr, manufactured by atomization, were analyzed by Nuclear Reaction Spectroscopy.

The total amount of oxygen appears to be high: about 1.8 to 2 wt%, for the samples pressed at room temperature and 1.2 wt% for the samples forged above 370 °C. These values correspond to alumina films formed during the atomization. All adsorbed oxygen and hydroxides are eliminated below 350 °C. The grain size influence appears only for the finest granulometry.

The $^{16}\text{O}(d, p) ^{17}\text{O}^*$ nuclear reaction is an efficient method for determining with a good accuracy the quantity of oxygen in pressed and/or forged aluminium pre-alloyed powders. N.R.A is non a destructive method, which allows the quantity of oxygen to be determined, independently of its chemical environment. It is of special interest when the material contains Al_2O_3 , which is a very stable species. Furthermore, analyzing the bulk material, the surface contamination will not disturb the results and the sample preparation is then simplified.

The basic set-up seems to be rather heavy (a particle accelerator), but the results are quite easy to obtain, and – this is of importance for the analysis – the measurements are short (about ten to twenty minutes) and then not expensive if the number of analysis to be performed would be high.

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