Characterisation of oxidised aluminium powder: Validation of a new anodic oxidation bench

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ABSTRACT

Aluminium powder is of major interest in many applications but it presents a risk due to its high explosibility, particularly when dispersed in air. The safety is directly linked to the particles oxidation because the Minimum Ignition Energy (MIE), which is required to initiate an Al dust explosion, increases with the oxide layer thickness. This study provides a controlled method to furnish reproducible homogeneous set of powder for such safety studies. Thanks to a new experimental bench, the influence on the oxidation rate of seven treatment parameters is investigated (current density, time of treatment, acid concentration, mass of powder, particles size, stirring, neutralisation by ammonia solution). The oxide content is plotted versus the current density, the time and the acid concentration to provide reference curves for further elaboration of oxidised powder. The particles size of sieved powder is measured before and after treatment by different methods (optical and Scanning Electron Microscopes, laser measurement). A high refinement of the powder in terms of size distribution is achieved thanks to the employed sieving. The present bench and the elaborated procedure are of great interest to provide well-calibrated oxidised powder directly available for safety studies. The time must be adjusted, depending on the wanted oxide content – from 2 to 18 wt.% – and the other treatment parameters must be kept constant: acid concentration (5 wt.%), current density (1 A dm^{-2}), treated powder (20 g). In these conditions, the ratio of the oxide layer thickness on the particles diameter is found to be constant for a given oxide content whatever the particles size.

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1. Introduction

The aluminium powder, from millimetric flakes to nanoparticles, is often used in various applications. A direct link exists between its initial oxidation state and its combustion properties; such as the Minimum Ignition Energy (MIE) and the flame velocity. The nanoscale is often related to propulsion applications [1] and pyrotechnic compounds because of the high burning rate of such small particles due to their high specific contact surface [2,3]. The nanometric powder also presents the advantage to reduce the waste after combustion [4]. Thus, it is replacing the micrometric one though this latest is still considered and characterised, mainly in terms of combustion [5]. But the micrometer particles are still found for applications like organic coating [8] even if the actual trend is to use smaller ones [6]. The microparticles represent about two orders more than the nano ones on the world market [9]. This justifies considering them; three others reasons are given below.

The oxide layer covering the particles is often undesirable because it causes them to be less reactive [10]. But it could be a source of safety. Geisler [11] gives the example of a motor which exploded due to violent combustion instabilities. This was attributed to the new aluminium particles, less oxidised, which were used. This is a first example for which it could be interesting to use aluminium particles with controlled oxide layer. This means of safety is notably studied for nanoparticles [12].

Another example using controlled oxide layer is linked to the physical and optical properties of the alumina which modify, through the light refraction, the perception of colours and shine of organic coating and paint [13]. It is possible to adjust the oxide layer thickness of aluminium particles used in painting to vary this esthetical effect.

Thirdly, alumina particles are also used in copper matrix that is intended to serve at high temperature [14,15]. The addition of Al or Al_2O_3 is investigated with nano- and microsized particles. For the authors, the addition of Al particles in copper matrix, then oxidised 20 h in air at elevated temperature, increases the microhardness. It appears to be the best combination of the thermal stability and electrical conductivity. Thus, providing a way to oxidise Al particles in few minutes could be interesting at larger Cu matrix production scale.

Finally, regarding numerous safety studies on aluminium particles (linked to the ATEX rule), the oxide layer thickness plays an

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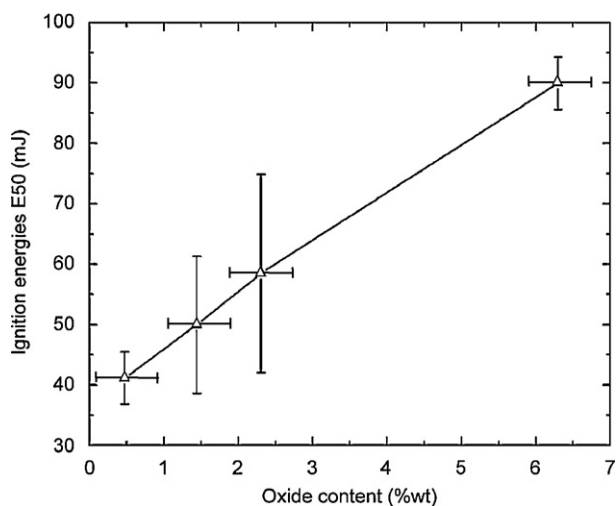*E-mail address:* Nicolas.Gascoin@univ-orleans.fr (N. Gascoin).

Fig. 1. Mitigation effect of the oxide content in the Al powder on the ignition energy [16].

important role on ignition [16]. Augmenting this thickness, thus the oxide content (Fig. 1), increases the E_{50} energy (50% of ignition probability as defined in [16]). No alumina is found in the core of the particles. This has been shown in previous work [16] thanks to EDS (Energy Dispersive X-ray Spectroscopy) analysis. The respective O and Al atomic percents are plotted along the particle diameter. The O atoms appear only near the surface. The ratio of Al and O atoms corresponds to the alumina formula (Al_2O_3) on the surface [16]. In the present study (like in [16]), the term "oxide content" refers to the oxide quantity that is found on the particles surface. The initial Al particles present a natural oxide layer of few nanometres, which is equivalent to an oxide content of about 0.5%. The oxide layer thickness can be increased artificially by anodic oxidation for example. This is a very well-known technique [8] for Al pieces of various shapes but it is rarely applied to powder because of the difficulty to provide a suitable electrical contact between the anode and the powder. It is thus necessary to supply a way of oxidising such Al micrometer particles by controlling the experimental treatment parameters in order to obtain the wanted oxide content on a given commercial powder. This is required in order to conduct experiments on Al safety in good conditions.

The previous work conducted by Baudry et al. [16,17] used an installation of surface treatment to oxidise the powder. In this further step, it is chosen to investigate in details the way to obtain suitable oxidised Al powder. A new dedicated anodic oxidation installation is presented for powder with a set of pre- and post-experimental procedures (sieving, particles size measurement, oxidation treatment, filtering). In this paper, the oxidation does not mean the combustion of the powder but only the particle surface conversion into alumina thanks to an electrochemical process in a sulphuric acid solution. The direct current form is used for the present work.

Some studies can be found in the literature on anodic oxidation of powder but always on compacted powder forming solid electrodes or pressed pellets [7]. This is not an appropriate method to obtain non-agglomerated powder for safety studies. The oxidation of non-agglomerated powder is found in the literature by means of fluidised bed in air for nanoparticles. To our knowledge, there is only one paper available in the open literature dealing with the anodic oxidation of Al micrometric powder [8]. The authors use two kinds of anode. The first one is a horizontal one in titanium on which the powder is laying; the second one is made of compacted Al powder linked by a water-soluble ligand, which is dissolved in the electrolyte during the process. The Al electrode shows the highest oxide content because of a better electrical contact. Nevertheless, a problem of oxidised Al powder homogeneity appears. It could be due to the repartition of electrical current lines and to the lack of stirring. The determination of oxide content is made by selective chemical dissolution. They observe that the oxide content reaches a limiting maximum value after 5 min for all the intensity value (from 6 to 10 A with very small electrodes surfaces, that is to say several hundreds of A dm^{-2}).

Fundamentally, the anodic oxidation of solid aluminium parts is well known. The oxide forming and growing are controlled mainly by ionic conduction owing to the electrostatic field produced in the oxide by the applied current [19,20]. The different interfaces (metal-oxide-solution) play a role in transfer processes. But no extension of these results is found for the powder oxidation in acid solution. Furthermore, it does not inform quantitatively on which treatment parameters should be used to obtain a given oxide content. The understanding of oxide growing on Al powder is a very complex phenomenon that is not investigated in this paper.

In the present study, we aim at establishing a detailed procedure to treat Al powder and to give reference treatment parameters to use in order to obtain the wanted oxide content. The improvements of the bench, compared with the previous one, are described and explained, such as the steps of the suggested experimental procedure. A design of experiments [21] has been used to estimate the influence of treatment parameters. This study is performed in the framework of Al powder safety. There is a direct link between the feasibility of the process and the determination of Minimum Ignition Energy of Al cloud in the laboratory.

2. Experimental

Baudry et al. [16,17] used a pedagogic installation of surface treatment to oxidise the powder. After characterisation by means of Thermogravimetry Analysis (TGA) and Scanning Electron Microscope (SEM), the powder was placed in a Hartmann apparatus [18] to test its explosibility [16]. The Hartmann tube applies compressed air at the bottom of apparatus to form dust cloud and to initiate it by an electrical spark (Fig. 2). In view of the difficulty to control the powder oxidation, Baudry et al. were not able to test samples with oxide content between 4 and 6 wt.% and between 7 and 9 wt.%. The authors estimated the uncertainties on the oxide content to be lower than ±0.573 wt.% for the initial unsieved powder [17]. This is reported in Fig. 1. The variation of the amount of oxide content was obtained by only adjusting the time; all other treatment parameters were uncontrolled.

We now intend in this study to investigate the influence of other treatment parameters. For this purpose, the sieving of powder allows obtaining the sets of Al powder with given size distribution. The samples are oxidised with fixed treatment parameters in the dedicated bench (Fig. 3). This latest is composed of a cylindrical glass tank of 2.5 L with concentric cylindrical Pb cathode and Ti anode. It is filled with sulphuric acid solution. An air or magnetic agitation is possible. The Al powder is enclosed in a porous bag to avoid its dispersion in the bath. The powder is then dried before measurements are done. This brief description is detailed in the following sections.

2.1. Sieving procedure of Al powder

The Al powder, which is used by Baudry et al. for the safety studies is a commercial micron sized aluminium powder (purity > 99.7%) supplied by the company "Métaux & Chimie" and referenced F3915 [16]. Its distribution presents a maximum fraction (5 vol.%) around 35 μm but also a peak near 7 μm (4 vol.%) [16]. An efficient way of sieving is required to provide homogeneous set of
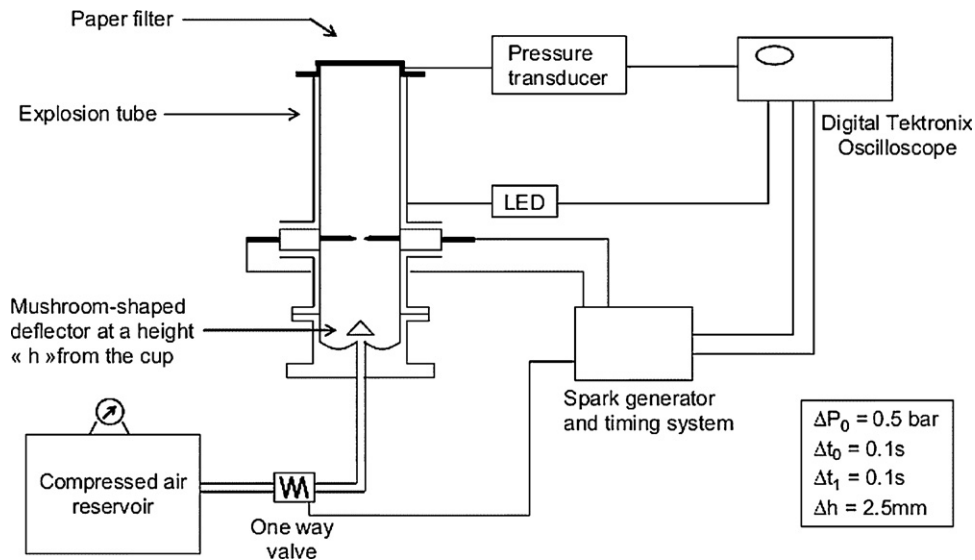
Fig. 2. Experimental bench with Hartmann tube used by Baudry et al. to test the explosibility of Al powder [16].

powder before testing the influence of the particles size on the oxidation. The homogeneity of Al powder set may also be correlated to the one of the treatment. Furthermore, the MIE determination may depend on the ratio of the oxide layer thickness on the Al particle diameter.

A new sieving method has been proposed to avoid the agglomeration of particles by electrostatic charging and to force the big particles through small sieves. Four sieves (20, 30, 40, and 50 μm) are assembled together and fixed on the vibrating table (4 s of moderate intensity vibrations by interval of 1 s). The powder is deposited in the biggest sieve and ethanol is poured on it to separate particles naturally (50 ml every 8–12 min). This allows sieving in less than an hour about 4 g of powder (required quantity for a statistical test of explosibility [17]).

2.2. Particles size characterisation and distribution

Three techniques are used to evaluate the distribution of particles depending on their size. The laser one is considered to be reliable but a former highly frequent bimodal distribution of Al particles [16] incites us to test other methods. The distribution of the particles, depending on their size, is expressed by the number of particles or by their volume, assuming they are spherical.
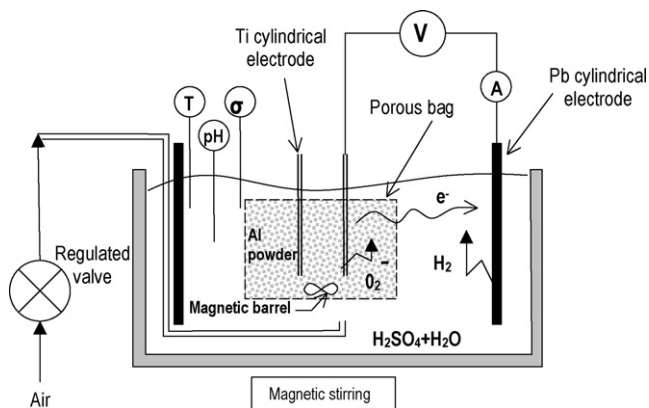

Fig. 3. Particles size distribution (in number) of sieved Al powder with a theoretical diameter: (a) lower than 20 μm, (b) in the range 20–30 μm, (c) in the range 30–40 μm, (d) in the range 40–50 μm.

2.2.1. Laser measurement

A laser diffraction technique (Malvern, Spraytec) is combined with a specific apparatus used to put in suspension the Al powder by air injection [17]. It has been shown that such measurement is reproducible. The main drawback is due to a possible agglomeration of particles.

2.2.2. Optical microscope

The optical microscope (Bausch & Lomb, MicroZoom), equipped with a video camera, is used with a statistical method to observe the Al powder. An adapted empirical procedure has been established after several trials to get reliable powder measurements. Fifty measures are realised and are available to estimate the distribution of particles size of a given sample of sieved powder.

2.2.3. Scanning Electron Microscope

The SEM (LEO, 1455 VP—Partial Vacuum) is used to observe the oxide layer thickness and to evaluate the diameter of Al particles. This gives the ratio of the oxide layer thickness on the particles diameter. By assuming the oxide is uniform around spherical Al particles, it is possible to compute the oxide content of the overall powder for comparison with TGA results. The preparation of samples is described in Ref. [17].

2.3. Surface treatment of Al powder

Formerly, the way to treat the Al powder for safety studies on aluminium particles [16] was to use an existing anodic oxidation bath of 50 L with six rectangular Pb cathodes (400 mm × 100 mm × 10 mm). The anode was composed of an aluminium honey spoon (thirteen Al disks with a central rod), filed with Al powder and closed in a textile bag. The sulphuric acid concentration was not verified (probably around 20 wt.%) and a constant voltage of 10–15 V was applied (current density of about 2 A dm^{-2}). The bench presented several drawbacks that are now corrected by the new apparatus.

A stirring in a smaller tank is used to avoid the particles agglomeration. The oxidation of the anode and the agglomeration of particles on it are solved by using a titanium electrode, whose standard electrical potential (-1.75 V at 298 K for Ti^{2+}) is lower than that of aluminium (Al^{3+}: -1.67 V). Other tests have been done with zinc anode (potential higher than aluminium: -0.76 V) and did not give much different results. The titanium anode and the Pb cathode are

now cylindrical (respectively 40 and 190 mm of diameter) in order to homogenise the repartition of the electrical current lines. The current density used in the paper is calculated by considering the anode surface and not the metallic powder one, which is obviously difficult to express.

To slow down the oxidation process, the sulphuric acid concentration in the bath is decreased even to 5 wt.% and the current density even to 0.5 A dm^{-2}. A high current density oxidises the powder in few minutes (about 12% after 5 min [17]), which is difficult to control. The quantity of Al powder introduced in the bath varies from 5 to 10 g because it is retained as a treatment parameter for this study. To have stable operating conditions, the intensity is kept constant by increasing the voltage to compensate the electrical resistance, which rises. Indeed, the electrical resistance of alumina is higher than the one of aluminium.

Even if the alumina does not significantly dissolve at room temperature without intensity; that may locally appear if the bath is not sufficiently stirred and if warm zones appear (over 300 K). A way to avoid alumina dissolution is to plunge the powder directly in ammonia solution after treatment in order to neutralise the sulphuric acid effect. That would allow observing the oxide surface with or without the neutralisation. The reproducibility issues encountered by Baudry et al. during ignition tests [17] may also be linked to the open porosity of the oxide layer and that may be tested by sealing alumina with hot water (95 °C).

Several parameters are monitored during the experiments to observe their variations and to evaluate their impact on the process (temperature, pH, electrical conductivity, electrical current and voltage). The voltage is regularly increased during the experiment in order to compensate the intensity decrease due to the electrical resistance of alumina.

2.4. Thermogravimetry analysis

The thermogravimetry analysis is commonly used to estimate the oxide content of aluminium powder [22,23]. A very good study on the alumina formation on Al particles is given by Trunov et al. [24]. Thanks to the TG apparatus (SETARAM, SETSYS 16/18 TG), the Al powder (sample of about 13 mg) is oxidised under air atmosphere. The mass of the sample increases by addition of oxygen, conducting to the transformation of Al into Al_2O_3. If the mass increase of the powder in the TG balance is lower than the theoretical maximum value for pure Al, it is due to the presence of alumina in the initial powder sample. The same parameters for the TGA as [16] are used (thermal increase at a rate of 20 K min^{-1} from 295 to 1863 K, then isotherm of 3 h). The determination of oxide content (detailed in [16]) is based on the comparison to a total oxidation of Al into Al_2O_3 by O_2, which conducts to a mass increase of 89%. This oxide content is the parameter used in all this paper to judge the oxidation of the powder. The coating ratio (mass ratio of oxide on Al) is equal to the unity plus the oxide content.

2.5. Parameters of treatment and design of experiment

The design of experiment has been used in order to propose a limited number of tests suitable to evaluate the implication of seven treatment parameters on the oxide content. These seven parameters and their two levels are given in Table 1. The low level is referred as − and the higher one as +. This will be important to compute the effect of each parameter on the results of oxide content. The treatment parameters are considered to be independent to use an Hadamard matrix of eight tests. This highly limits the number of experiments but it does not allow evaluating the possible interactions of treatment parameters. The result under study for the design of experiment is the final oxide content of treated Al powder.

Table 1
The seven selected parameters for the design of experiment with their two levels.

Number	Parameters	Levels	
	Denomination	Low (−)	High (+)
X_1	Time of treatment (min)	10	60
X_2	Electrical current density (A dm^{-2})	0.5	2
X_3	Sulphuric acid concentration (mass% in water)	5	20
X_4	Particles size distribution (μm)	[20–30]	[40–50]
X_5	Stirring	Without	With
X_6	Mass of powder (g)	5	10
X_7	Neutralisation by ammoniac	Without	With

The influence of the three main parameters has been further studied to provide suitable reference curves for future oxidation treatment. Some results on successive sieving will be given in the next section. After treatment, the oxidised Al powder is immersed in ammonia solution or deionised water to evacuate the sulphuric acid before rinsing and filtering in paper. The powder is then dried two days in air atmosphere at 353 K. The titanium electrode is cleaned by corundum projection to evacuate any kind of oxide and then rinsed in ethanol with ultrasonic.

3. Results and discussion

The particles size is of great interest because the present study must determine if the oxidation activity of powder depends on this parameter. It also allows computing the ratio of the oxide thickness on the particles diameter for different oxide content and different size of particles. This could be a key point in the safety studies to understand the explosibility tests.

3.1. Particles size distribution

After counting the number of particles corresponding to several size ranges, it is possible to plot the resulting powder distribution. That can be done for the initial unsieved powder but also for each sieving range corresponding to the size of the sieves. By assuming the particles are spherical, the number of particles of a given diameter can be interpreted by its volume (in m^3). The distribution of particles can thus be given in terms of number of particles or in terms of their volume. We will see that this is far to be similar.

3.1.1. In terms of number

The sieved Al powder is observed by optical microscope and by laser technique (Fig. 4). The results are expressed, for a given particles diameter range, in percent of the particles number of this range related to the overall particles number. The powder obtained with the sieve of 50 μm size is not considered because its explosion risk is too low [16]. The optical method enables to detect and to measure very fine particles (smaller than 5 μm) while the laser one does not because of a lack of accuracy and because of an agglomeration of these particles. But with 50 measures, the visualisation presents the limitation of the counting with statistical errors for the biggest particles. This is not the case with the laser because it performs several hundreds to thousands of measures. Nevertheless the laser results on biggest particles can be questionable as they can be due to agglomeration of small particles.

The optical measurements, qualitatively better, reproduce the particles size increase from Fig. 4a–d compared to the laser technique. Indeed, no particles over 10 μm are detected in Fig. 4a (for powder sieved under 20 μm) while about 10% are detected in Fig. 4d (powder in the range 40–50 μm). The maximum peak of small particles in the range 5–10 μm decreases continuously from 78% (Fig. 4a) to 52% (Fig. 4d). Nevertheless, these results, which are related to the
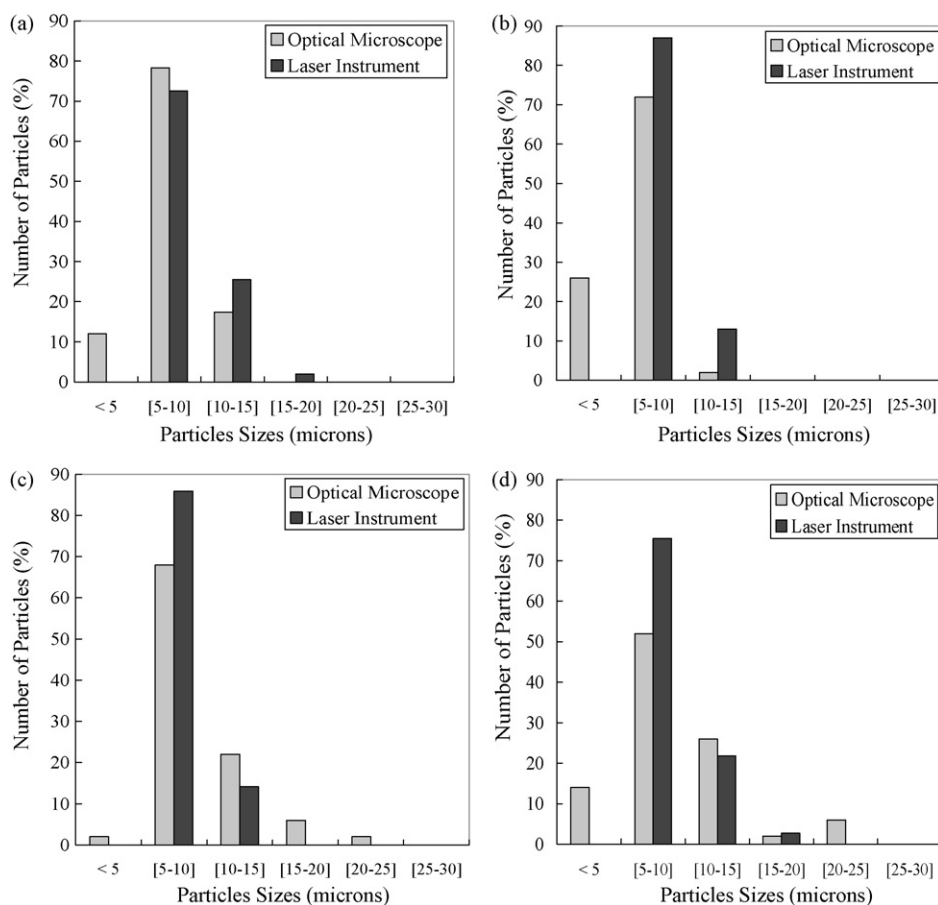
Fig. 4. Particles size distribution (in volume) of sieved powder with a theoretical diameter: (a) lower than 20 μm, (b) in the range 20–30 μm, (c) in the range 30–40 μm, (d) in the range 40–50 μm.

number of particles counted for each size, do not correspond to the sieves sizes.

The necessity of sieving is clear. One can observe that for a given range of sieving, for example 20–30 μm (Fig. 4b), no particle is found in this range with both optical and laser methods. All the particles present smaller diameters. This is also due to the fact that very small particles (less than 10 μm) are much more numerous than others. Consequently, the sieving does not allow refining a powder if the distribution in term of particles number is of interest. But thanks to this work, it is possible to estimate the uncertainties on the particles diameter.

3.1.2. In terms of volume

As the high number of small particles perturbs the counting, the size distribution is studied in terms of volume (Fig. 5). The small particles, even numerous, represent a small volume compared to the one of big particles. The particles which are smaller than 10 μm are still widely present but they are now in minority. Furthermore, the relative importance of the fine particles peak decreases while the sieve size increases, which is satisfactory. The reference peak corresponds to the size of the sieve and it should be predominant. Nevertheless it is the case only for the biggest sieve, and not for the others. This peak is centred on the particle diameter of 22 μm for the powder sieved under 20 μm (Fig. 5a), 24 μm for the range 20–30 μm (Fig. 5b), 27 μm for the range 30–40 μm (Fig. 5c) and 46 μm for the range 40–50 μm (Fig. 5d). These results are judged acceptable but the successive sieving can bring a better separation to provide a volume majority for the reference peak.

3.2. Successive sieving

To refine the particles size distribution of initial Al powder, several successive sievings have been realised to "purify" the samples. An example is shown for the powder sieved in the range 30–40 μm (Fig. 6). The magnitude ratio of small particles peak on the reference peak decreases drastically from $9.3/7.2 = 1.29$ (Fig. 6a), to $7.2/7.9 = 0.91$ (Fig. 6b), to $6.3/9.1 = 0.69$ (Fig. 6c). A sieved powder largely representative of the sieving range is obtained, here 30–40 μm. The maximum of the reference peak, initially found around 27 μm, passes to 32 μm then 30 μm after the second and third sieving.

During these successive sievings, the initial powder mass obtained in the range 30–40 μm has been divided by a factor 5. From the original 32.9 g of 30–40 μm powder, 17.8 g was collected after the second sieving in the same range while 6.7 g shows a particle diameter lower than 30 μm and 6.6 g a diameter higher than 40 μm. According to the mass balance, 1.8 g is found to be lost in the overall sieving and filtering process, that is to say 5% of the initial powder mass. Then after the third sieving, 6.2 g is in the range of study.

3.3. First results of design of experiments

The measurements made during the anodic oxidation show almost constant values. The temperature remains between 291 and 298 K, depending on the room temperature. It slightly increases during the process (not more than 2 K). The pH is near 1.5 and the electrical conductivity is also stable but it depends on the exper-
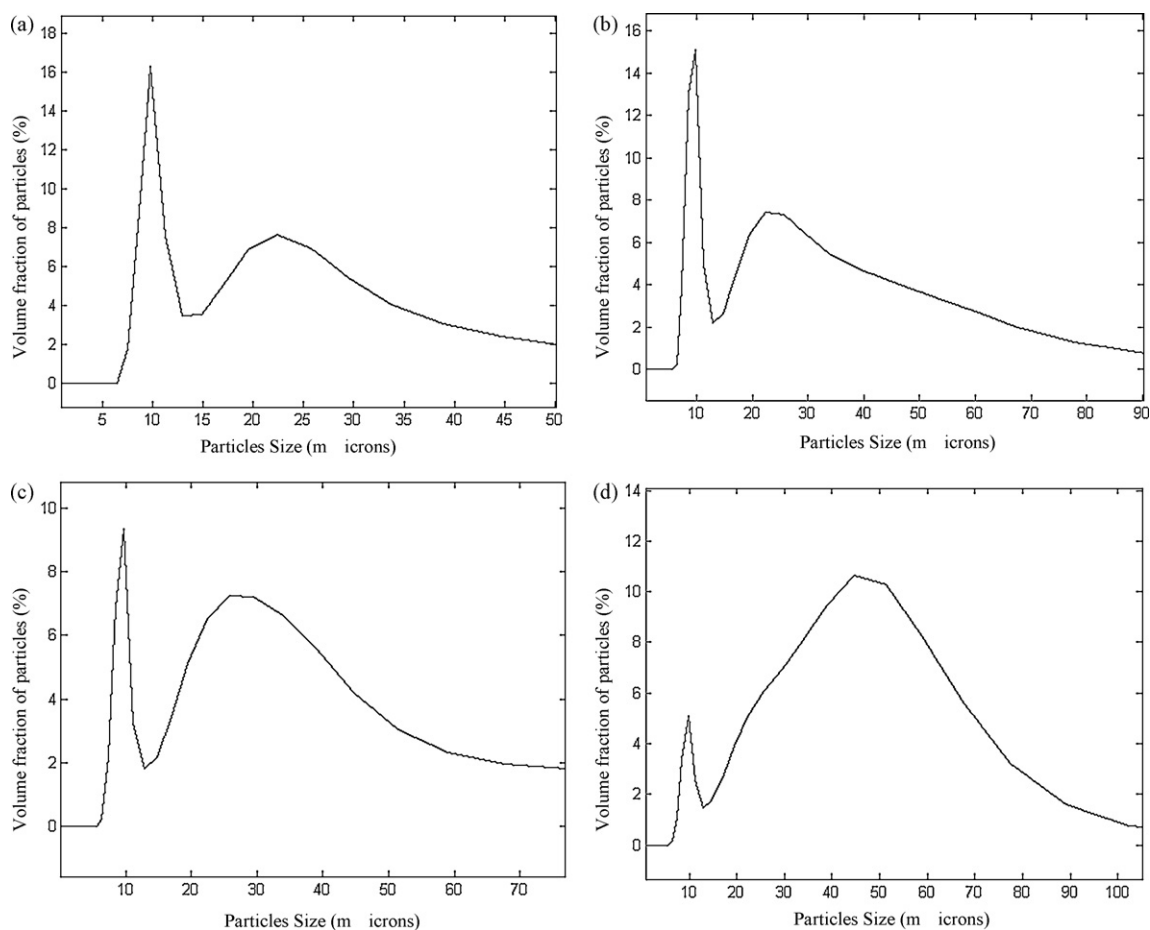
Fig. 5. Particles size distribution (in volume) of sieved powder in the range 30–40 μm after one sieving (a), two sieving (b) and three sieving (c).

imental test conditions because it is related to the sulphuric acid concentration (from 150 to 600 mS). The intensity is kept constant during the treatment to fit the desired current density (computed based on the anode surface) and the resulting voltage changes from 10 to 25 V depending on the test and the oxidation of powder. The quantity of powder, which is obtained after the treatment, the rinsing, the filtering and the drying of Al powder, has been increased through the successive experiments. From an initial mass of 5 g, 4.8 g is finally gathered (4% of loss in the successive steps).

The results of the design of experiment are summarized in Table 2. The Hadamard matrix is constituted of seven columns and eight lines, corresponding respectively to the seven treatment parameters to be tested and to the eight experiments recommended by Hadamard. The seven parameters are considered with their low level noted "−" and their high level noted "+" (with the values given by Table 1). The oxide content (unit: vol.%) which results from each of the eight tests is measured by TGA and it is noted by Y_i ($i = 1, . . ., 8$). The influence (noted b_i, i = 1,. . .,7) of each parameter is computed by adding all the results Y_i. Each of them is multiplied by the related level of the considered parameter (low or high), that is to say −1 or +1. The term b_0 is the sum of all the effects b_i ($i = 1, . . ., 7$). The more the effects b_i are far from 0, the more they influence the oxide content. The particles size distribution has a limited impact on the oxidation process. This is understandable because the oxidation is mainly controlled by the electrical phenomena. But the size distribution can play a role on the oxide thickness on particle diameter ratio and this will be studied in the next section.

Thanks to this design of experiment, it is firstly seen that the mass of powder which is treated does not influence notably the

oxidation process. Considering the same treatment parameters, the more the powder, the less the oxide content. The current density should be increased with the powder mass to reach the same oxide content. These two parameters may not evolve proportionally. The stirring also does not impact on oxidation for the same reason. But these two last parameters can impact on the homogeneity of the oxidised powder sample and this cannot be observed by simply measuring the oxide content. The SEM visualisations or the ignition tests (safety study) could bring further information.

The current density and the sulphuric acid concentration appear to be the most important treatment parameters regarding their respective results $b_2 = 22.91$ and $b_3 = 23.16$. This is due to the fact that the process is electrochemical by nature. An interaction of these two parameters is possible but it cannot be taken into account in these first eight tests. Consequently, a more detailed study has been realised to identify the implication of both parameters in the oxidation of powder.

The neutralisation of oxidised powder by ammonia solution just after treatment is surprisingly the third most important parameter. Neutralising the powder helps keeping the oxide layer by avoiding its dissolution in the acid bath between the stop of intensity and the powder outlet of the bath. But this effect is questionable because it does not increase the oxide content of the powder. Thus, it is impossible to compare its effect to the intensity or the electrolyte electrical conductivity. In the design of experiment, there is a common "law" of 80–20%. That means that only 20% of the parameters are really influent on a process. Now three parameters out of seven correspond to 43%. This shows that the effect of the third parame-
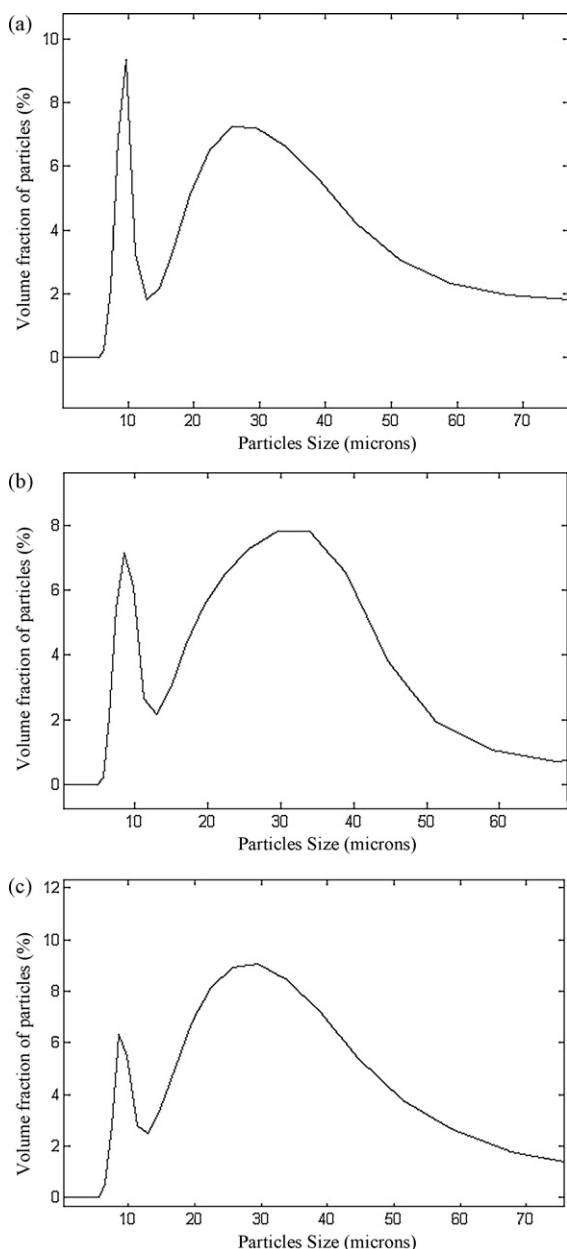
Fig. 6. Effect of the acid concentration on the oxide content.

Table 2
Hadamard matrix of experimental tests with oxide content results and influence of parameters.

Test number	Numebr of the parameter							Results	Oxide content (%)
	X_1	X_2	X_3	X_4	X_5	X_6	X_7		
1	+	+	+	−	+	−	−	Y_1	15.77
2	−	+	+	+	−	+	−	Y_2	10.29
3	−	−	+	+	+	−	+	Y_3	0.85
4	+	−	−	−	+	+	−	Y_4	1.55
5	−	+	−	−	+	+	+	Y_5	2.44
6	+	−	+	−	−	+	+	Y_6	3.54
7	+	+	−	+	−	−	+	Y_7	1.8
8	−	−	−	−	−	−	−	Y_8	1.5

Effects from b_0 to b_7 corresponding to the influence of the parameters

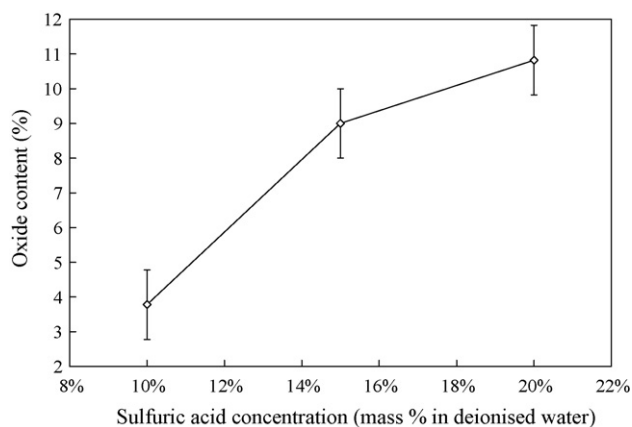| b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_0
7.58	22.91	23.16	−8.76	3.48	−3.50	−20.48	37.74

Fig. 7. Effect of the time of treatment on the oxide content.

80 wt.%). The uncertainties on the acid concentration are judged to be negligible (0.01% of accuracy). The rapid evolution of the oxide content in the range of 10–15 wt.% of acid in the bath highlights the fact that a low acid concentration should be used to precisely control the oxidation rate. This is confirmed by studying the influence of the time of treatment (Fig. 8). Due to the high acid concentration (20 wt.%), the oxide content is multiplied by a factor 5 in only 5 min (from 5 to 10 min of treatment). The rate of oxidation remains slightly constant from 10 to 60 min of treatment ($0.1\,\mu m\,min^{-1}$). This is one order less than the one generally observed for the anodic

ter, the ammonia solution one, is only due to an interaction of the two others.

The time of treatment is not shown to be very influent on the oxide content and this is probably the limitation of such a simple design of experiment matrix. The low level (10 min) may not be well chosen due to the rapidity of the oxidation. This point needs to be studied in details; that is why other specific tests have been realised to precisely investigate the effect of time.

3.4. Influence of treatment parameters on anodic oxidation

The oxide content (defined as the percentage of alumina found by TGA in the oxidised Al powder, see Section 2.4) of treated Al powder does not vary linearly with the sulphuric acid concentration (Fig. 7). It is attributed to the nonlinear evolution of the electrolyte electrical conductivity, which presents a Gaussian trend centred on 25 wt.% (roughly 150 mS at 5 wt.%, 600 mS at 25 wt.% and 100 mS at
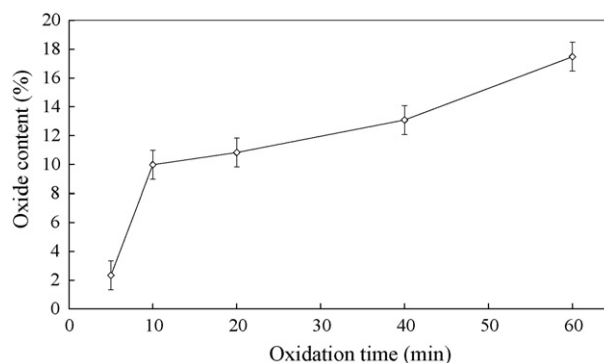

Fig. 8. Effect of the current density on the oxide content.
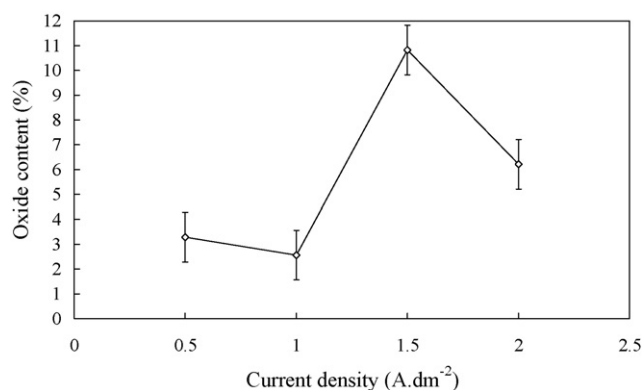
Fig. 9. Oxide content of sieved powder treated with the same test parameters.

oxidation of solid aluminium parts. The variations can be attributed to the average efficiency of the manual intensity adjustment. The uncertainties on the oxidation time are of the order of 2 s, that is to say lower than 0.67%.

The current density, which is estimated with an accuracy of 6.7% (Fig. 9), presents an optimum in terms of oxide content around 1.5 A dm^{-2}. For higher value of 2 A dm^{-2}, lower oxide content is observed. This is attributed to the "burning" phenomenon, which corresponds to a thermal increase near the anode. This is accompanied by a lower efficiency of the anodic oxidation.

Finally, the oxide content is measured for the same experimental conditions as a function of the particles size distribution (Fig. 10). Due to the uncertainty on the oxide content estimation (about 1%), it is difficult to evaluate if the particles size distribution has an impact on the oxide content. It is assumed that this distribution does not impact on the oxidation. Thus, the three points on Fig. 10 correspond to sample with identical oxide content. Consequently, it is interesting to observe the oxide layer thickness on these samples to estimate the ratio of oxide thickness on particles diameter. This point is further studied in the Section 3.5.2.

3.5. Evaluation of the oxide layer thickness

3.5.1. Indirect measurement

The maximum oxide content observed during the present experiments is about 18%. It is obtained for powder in the range 30–40 μm with 1 A dm^{-2} and 20 wt.% of sulphuric acid. Considering spherical particles with uniform oxide layer, this oxide content should correspond to a thickness of 2.1 and 2.8 μm for an Al particle diameter of
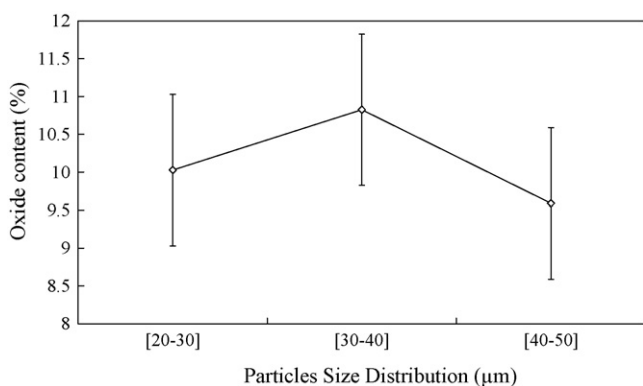

Fig. 10. Particles size distribution before (a and c) and after (b and d) the oxidation treatment of sieved powder in the range 20–30 μm (a and b) and 30–40 μm (c and d).

30 and 40 μm respectively. This should modify the particles size distribution. This one is thus measured by the laser techniques (whose resolution is finer than 1 μm) on two ranges of sieved powder; before and after the oxidation treatment (Fig. 11). After treatment (Fig. 11b), the 20–30 μm powder presents an inferior number of small particles (around 10 μm) than before (Fig. 11a). This could indicate an agglomeration during the oxidation. The maximum of the reference peak is slightly shifted towards the biggest particle. Its maximum is found at 26 μm while it was at 24 μm initially (Fig. 11a). If this 2 μm is attributed to the oxide layer, the resulting oxide content can be computed to be 25.6%. This is much more than the one measured by TGA (10.1%). The qualitative trend of the particles size increase cannot be exploited quantitatively because of the low accuracy of the overall laser measurement method. Concerning the 30–40 μm powder (Fig. 11c), approximately the same amount of small particles around 10 μm is found. The reference peak is also slightly shifted (Fig. 11d) by 2 μm (maximum found at 29 μm in comparison with 27 μm initially). The oxide content can then be computed (23.8%) and compared to the measured one by TGA (10.9%). Once again, a quantitative exploitation seems to be impossible.

3.5.2. Direct measurement

Three powder samples (20–30, 30–40, and 40–50 μm) are observed with the SEM (the same which were analysed with TGA to obtain Fig. 10). The oxide layer thickness and the particle diameter are measured for several particles (one example is given by Fig. 12). The ratio of these two parameters is calculated. The oxide content is evaluated by assuming spherical particles with uniform oxide layer (Table 3). A high difficulty to precisely evaluate the oxide layer thickness (up to 50% of uncertainty) is encountered as well as a dispersal of the particles diameter measures (up to 25%) owing to a low distribution homogeneity. The measures on SEM visualisation present the same statistical drawback as the one previously described for the optical microscope. These too low accuracies are mainly due to the poor number of measures (only six), which are more difficult because of the SEM technique itself. The method employed to prepare the Al powder samples should also be revised, notably by using a more conductive resin, prepared at high temperature. Furthermore, by using an electrically charged resin, it may be possible to use an electro polishing instead of a mechanical one, which separates the Al particles from the surface.

Thus, the quantitative exploitation of the data is hazardous (more than 100% of uncertainty of computed ratio and oxide content). But the main qualitative interesting point is the following. For a given oxide content, the ratio of oxide layer on particle diameter is the same for all the sieved powder. This can be easily confirmed by theoretical calculations of uniform layer around spherical particles. Consequently, the homogeneity of sample is shown to be of prior importance because if all the particles present the same oxide content, whatever their size, they will present the same oxide/diameter ratio, which is assumed to control the explosibility of powder [17]. The importance of sieving is again shown here.

Table 3
Determination of the oxide content based on SEM observations.

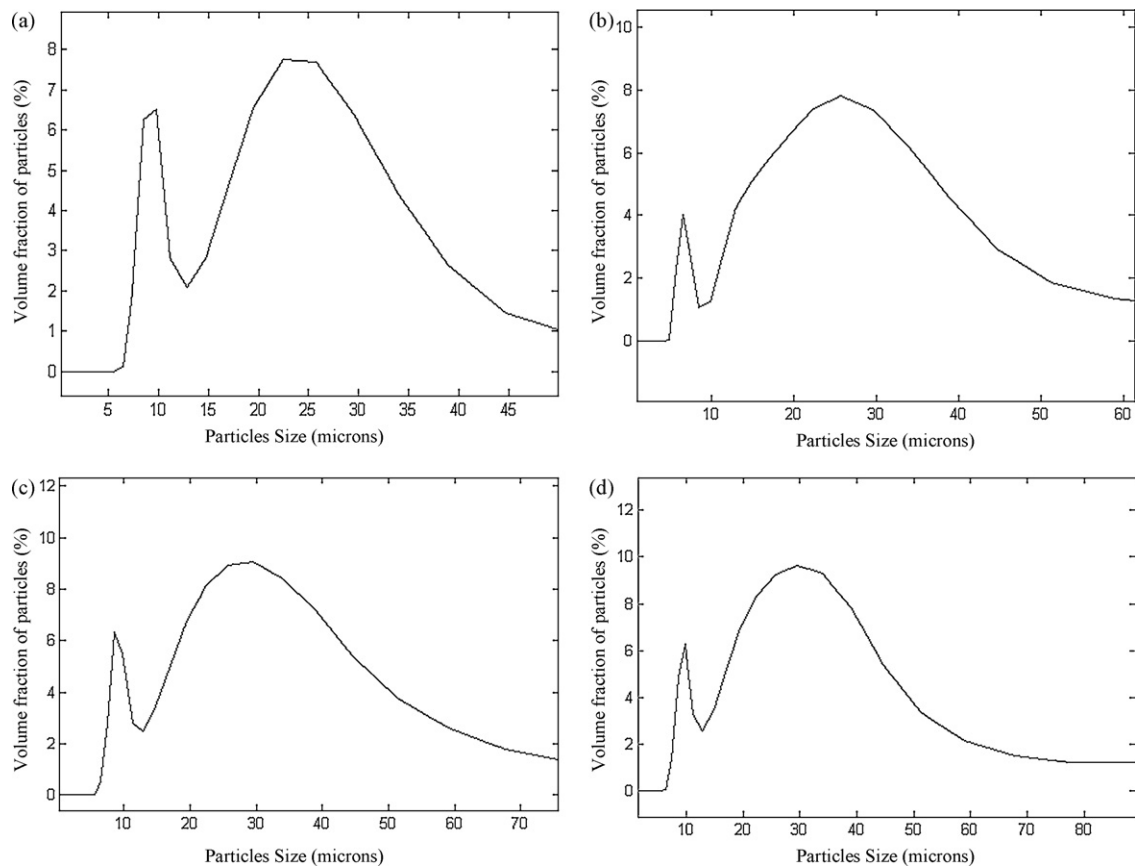|	20–30 μm	30–40 μm	40–50 μm
Particles diameter (μm)	21.03 ± 2.57	17.10 ± 3.89	23.57 ± 3.87
Oxide layer thickness (nm)	239 ± 65	311 ± 109	455 ± 227
Ratio of oxide thickness on particle diameter	0.011 ± 0.005	0.018 ± 0.014	0.019 ± 0.016
Oxide content (%)	4.82 ± 1.78	8.06 ± 4.12	8.28 ± 4.86

Fig. 11. SEM visualisation of Al micrometric particle with oxide layer.
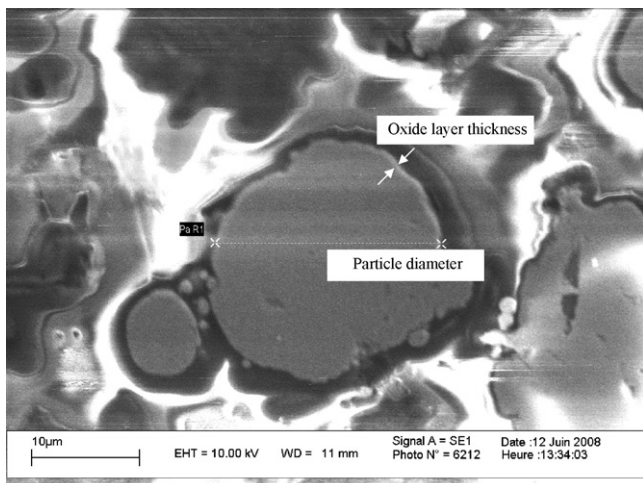

Fig. 12. SEM visualisation of Al micrometric particle with oxide layer.

4. Conclusions

An experimental set-up has been proposed to oxidise a commercial aluminium powder with a reproducible and controllable method. It has presently no equal in open literature due notably to the difficulty of establishing an electrical contact between the powder and the electrodes. The initial Al powder has been sieved in three particles size ranges to study their oxidation (20–30, 30–40, and 40–50 μm). The successive sieving allows refining the powder by more than a factor two. The electrode material is the titanium, the geometry of both electrodes is cylindrical to have a better elec-

trical current lines repartition, the stirring of the bath is proposed, a neutralisation by the ammonia solution is possible and other parameters than only the time of treatment have been investigated to vary and to control the oxide content of Al powder (current density, acid concentration, mass of treated powder, particles size distribution).

A design of experiment has been established and the major influence of some parameters has been shown: the time of treatment, the sulphuric acid concentration, the current density. A more detailed study of the relationship between these parameters and the oxide content has been conducted to establish three reference curves, which can now be used to estimate the oxide content for future treatment. Considering all the above work, the best parameters for the Al powder oxidation are: an acid concentration of 5 wt.%, a current density of about $1\,A\,dm^{-2}$, with a stirring, a neutralising by ammonia solution, an amount of powder of about 20 g for the described treatment apparatus. The quantity of 20 g is compatible with the amount required to conduct safety studies and to determine the Minimum Ignition Energy as a function of the oxide content. The time of treatment should be varied depending on the wanted oxide content. Due to the nonlinear effect of the treatment parameters on the oxidation, it is not possible to literally compute or predict the oxide content, based on the parameters level.

The particles size distribution has been measured before and after the treatment. The oxidation is shown to be qualitatively visible through this distribution. The oxide content has been computed thanks to TGA measures. It ranges from 2 to 18 wt.% depending on the treatment parameters. The SEM has also been used to estimate this information and to evaluate the oxide thickness, from to 174 to 682 nm. This way of determination appears to be feasible even if the accuracy is much lower than that of TGA data. Nevertheless, the main advantage of SEM observations (beyond the fact that it

shows the uniform oxide layer around each particle) is to evaluate the ratio of the oxide layer thickness on the particle diameter. This ratio appears to be slightly constant (for a given oxide content) whatever the initial particles diameter.

It has been mentioned that depending on the alumina thickness of Al particles, it could be possible to control the explosibility, and so the risk of this powder. The present bench (with the described optimised method for oxidising the Al powder) will be used in order to provide the required samples with oxide content that are missing to complete Fig. 1. If a given level of safety is wanted for an industrial configuration, this figure can be used to estimate the required oxide content of the Al powder. Our research gives the relevant experimental parameters to reach the wanted oxide layer thickness in order to inhibit the Al powder explosion.

Acknowledgements

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