

Research Article

The Transfer of Substance of Recycled Aluminum Utensils When Cooking Rice or Tomato in Senegal

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Abstract: This study focuses on the study of the behavior of aluminum alloys based utensils in Senegal against some daily food products such as rice (main cereal consumed) and tomato. The results of experiments show that these alloys, which do not respect the current standard NF EN 601 of July 2004, are generally more degraded when cooking foods aforementioned than the control sample which respects it. Mass losses are significant and go up to 0.2 mg/cm²/h for rice, as they are barely detectable for tomato. The mechanism of corrosion was exposed and appears to be related to the microstructure and chemical composition of the alloys. The presence of metallic ions is also detected in the substrates. Thus, given the daily use of these utensils to prepare more often rice, the issue of health consequences arises. A work with specialists health care partners is ongoing. However it would be interesting to see in future studies how to limit this degradation against rice.

Keywords: Aluminum alloys, recycling, rice, Senegal, tomato, utensils

INTRODUCTION

In Senegal the preparation of meals is mostly done using cooking utensils made by craftsmen. Alloys used resulting from the automotive industry, should not be used for the manufacture of kitchen utensils.

Previous studies have shown that most of these alloys do not respect the standards such as EN 601 and must therefore not be used in the food industry (Ndiaye *et al.*, 2012).

Rice is the main cereal cooked with these utensils. It is therefore useful to study the behavior of these alloys when cooking the rice. We completed this cereal by tomato that is also important in the kitchen in Senegal.

For this study an experimental protocol was developed and has allowed us to measure the effect of degradation through mass loss, micrographics and chemical analysis of the substrates.

The corrosion of the aluminum is widely studied (Davis, 1999). Studies of the corrosion of super alloys specially designed aluminum industry are numerous (Vasilescu and Vasilescu, 2009; Bean, 1995). However, studies are much less numerous in the food area of concern. Moreover, in this case, the work focus on the food brought into contact with the materials from which

it attempts to value the transfer. And a linking of two aspects of the problem is quite innovative.

MATERIALS AND METHODS

A study of several years, dozens of representing different alloys developed for manufacture utensils samples were collected. The analysis of the chemical composition of these samples was conducted in a previous study (Ndiaye *et al.*, 2012).

Among the multitude of craft alloys, we have chosen, based on their chemical composition, two alloys (Ech 01 and Ech 03), a pure aluminum plate and aluminum pressure cooker bought in France, which serves as reference. The samples were designated as follows:

- Ech 01, which contains low contents of silicon and copper in combination with high levels of magnesium
- Ech 03, which differs from the preceding by high levels of silicon and copper with a low magnesium
- (99.9%) pure aluminum called "Alupur"
- Reference sample, called "Ref" that was developed in Europe following the standard NF EN 601 of July 2004, which refers to the subject

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Table 1: Chemical composition

Mass (%)	Si	Cu	Fe	Zn	Mg	Mn	Cr	Ti	Pb	Sn	Ni	Al
Ech 01	2.96	0.837	0.726	0.730	0.748	0.204	0.0168	0.0110	0.0418	<0.0030	0.0836	Rest
Ech 03	8.33	3.430	0.777	0.602	0.183	0.172	0.0300	0.0512	0.0937	0.0246	0.1890	Rest
Alupur	<0.01	<0.010	<0.010	<0.010	<0.010	<0.010	<0.0100	<0.0100	<0.0100	<0.0100	<0.0100	Rest
Ref	0.17	<0.005	0.620	0.032	<0.010	<0.005	<0.0050	0.0160	<0.0200	<0.0200	<0.0050	Rest

The Table 1 recalls the composition of these samples used for testing culinary environment.

These samples come in two forms:

- Plate parallelepiped approximately 2 cm square and 2 mm thick, one surface of which was prepared by polishing. This allows us to follow the evolution of the surface under the action of different backgrounds. These plates also serve to follow the evolution of the mass loss of the samples during the various tests.
- Chips collected by turning from our raw samples. We used them during testing to quantify the mass transfer (colorimetry and plasma spectrometer) to increase the contact area with the environment. For an average chip thickness of 0.1 mm, the available surface area is about 74 cm²/g of alloy:

$$S_1 = 2 \times \frac{\text{mass of shaving (1g)}}{\text{volumical mass}} \times \frac{1}{\text{thickness of shaving}} = 74\text{cm}^2$$

In this way, when a rectangular sample of 2 mm thickness and 3 g of chips of the same material are placed in contact with the test solution in a pyrex vessel, the total surface in contact with the material is about 231 cm²:

$$S_2 = 2 \times 2\text{cm} \times 2\text{cm} + 4 \times 2\text{cm} \times 0.2\text{cm} = 9.6\text{cm}^2$$

To mount an operation simulating the Senegalese cuisine, we placed the samples in vials pyrex containing the following media:

- **OR:** Fifteen gram of flavored broken rice in 250 mL of tap water in boiling point
- **TF:** Fifty gram of fresh tomato mixed and transformed into tomato puree brought to boiling
- **CT:** Tomato paste (30 g of tomato concentrate at 28% added with 100 mL of tap water brought to boiling)

To avoid the many sources of dispersion inherent in tests performed in the food industry, the following experimental protocol was developed and implemented:

- The plate and 3 g of chips are immersed in a pyrex vessel containing one of the media identified above.
- At the end of each cooking cycle (15+15+30 min), during which additions of distilled water offset losses due to evaporation, the parallelepiped

sample is removed and rinsed in distilled water and then with alcohol in an ultrasonic bath.

- The cleaned sample is then placed in an oven at 110°C for half an hour at least, to remove any moisture before being weighed with a precision balance (the result is reported to the surface initial), then observed under an optical microscope, Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM).

The local surface analysis, done using the AFM after each test step can map the surface relief and provide more detailed information on the formation of cavities and the behavior of different phases during corrosion. Furthermore, roughness values can be obtained from these analyzes we used among which the index R_q . This statistical parameter R_q is defined as the mean square deviation of the profile, that is to say the root mean square value of the heights of the profile within the limits of the basic length. According to ISO 4287 is equal to:

$$R_q = \sqrt{\frac{1}{l} \int_0^l Z^2(x) dx}$$

where, $Z(x)$ represents the coasts of roughness profiles.

Colorimetry has allowed us to highlight the presence of ions in the substrates. For example through the tricarboxylate aurin ammonium or aluminon in a little acid solution, the presence of Al³⁺ ion gives a red colloidal compound. To avoid false positives, all hazard precautions given in the reference book (Charlot, 1963) were observed.

Finally substrate samples were also analyzed by the method of optical emission spectroscopy in an inductively coupled plasma.

RESULTS

The results obtained mainly concern the micrograph, the mass change and analyzing ions present in the substrates.

Micrographs: The observation micrographs of all the samples shows that the OR environment has caused a significant deterioration of the surface samples (Fig. 1), contrary to solution CT and TF (Fig. 2).

Mass loss and roughness: Micrographs observations were confirmed by the results for the roughness (Table 2) and variations in the mass per unit surface area (Table 3).

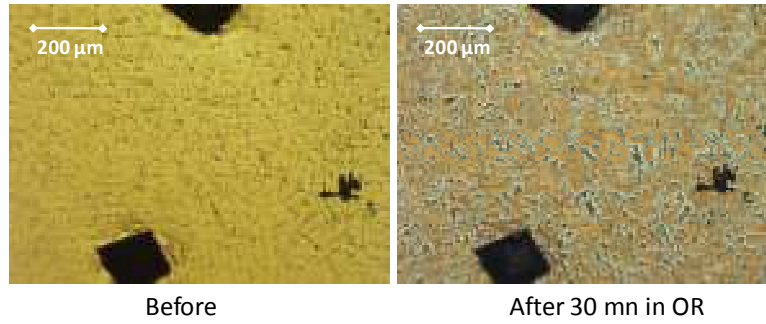


Fig. 1: Micrography of Ech 03 before and after corrosion in 30 mn in OR

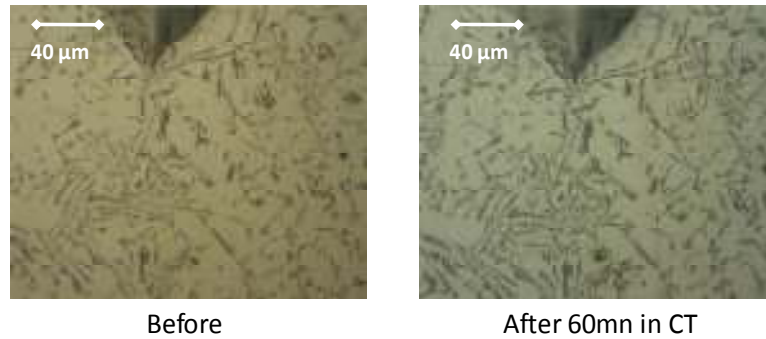


Fig. 2: Micrography of Ech 03 before and after corrosion in 60 mn in CT

Table 2: Evolution of R_q

Time (mn)	Alupur	Ech 01	Ech 03	Ref
Evolution of R_q (nm) in OR				
0	145.10	14.82	14.12	140.60
15	113.30	340.80	54.34	1233
30	247.30	250.20	193.40	1204
60	472.10	612.30	368.40	1321
Evolution of R_q (nm) in CT				
0	18.70	54.30	33.20	63.60
15	22.20	49.45	34.70	65.20
30	21.34	52.30	29.90	61.30
60	20.78	51.24	31.52	60.25
Evolution of R_q (nm) in TF				
0	39.22	19.50	27.40	60.35
15	36.98	22.56	25.50	62.21
30	38.64	18.50	29.30	57.83
60	40.39	20.40	26.53	59.50

Table 3: Evolution of mass/surface (mg/cm²)

Time (mn)	Alupur	Ech 01	Ech 03	Ref
Variation of the mass/surf (mg/cm ²) in OR				
0-15	0.034	0.0270	0.133	0.039
0-30	0.102	0.0550	0.163	0.155
0-60	0.176	0.0730	0.214	0.206
Variation of the mass/surf (mg/cm ²) in CT				
0-15	0.015	0.0170	0.025	0.027
0-30	0.019	0.0240	0.031	0.035
0-60	0.025	0.0029	0.038	0.039
Variation of the mass/surf (mg/cm ²) in TF				
0-15	-	-	-	-
0-30	-	-	-	-
0-60	-	-	-	-

Roughness: The Table 2 shows the different values of parameter R_q on the same profile during the test.

Table 4: Colorimetry

Ions detection by colorimetry after 60 mn				
	Al ³⁺ (mg/L)	Cl ⁻ (mg/L)	Fe ²⁺ (mg/L)	Cu ²⁺
OR: pH (7.7 before-8.2 after)				
Alupur	15	-	-	-
Ech 01	20	-	-	-
Ech 03	35	-	-	-
Ref	20	-	-	-
CT: pH (4.7 before-4.9 after)				
Alupur	50	600±50	-	-
Ech 01	50	600±50	-	-
Ech 03	60	600±50	-	-
Ref	30	600±50	-	-
TF: pH (4.7 before-4.8 after)				
Alupur	-	-	-	-
Ech 01	-	-	-	-
Ech 03	-	-	-	-
Ref	-	-	-	-

Table 5: Spectrometry

Ions detection by spectrometry after 60 mn				
	Al ³⁺ (mg/L)	Cl ⁻ (mg/L)	Fe ²⁺ (mg/L)	Cu ²⁺
OR: pH (7.7 before-8.2 after)				
Alupur	47±1.4	-	-	-
Ech 01	50±1.5	-	-	-
Ech 03	31±1.0	-	-	-
Ref	22±0.7	-	-	-
CT: pH (4.7 before-4.9 after)				
Alupur	66±2.0	550±50	-	-
Ech 01	76±2.3	570±50	-	-
Ech 03	107±3.2	560±50	-	-
Ref	67±2.0	600±50	-	-
TF: pH (4.7 before-4.8 after)				
Alupur	22±0.7	-	-	-
Ech 01	17±0.5	-	-	-
Ech 03	26±0.8	-	-	-
Ref	24±0.7	-	-	-

Mass loss variation: The measurements of the variation of the mass have been reported to the surface considered and are given by the Table 3.

Chemical analysis of the substrates: Chemical analysis of the substrates after the test reveals the presence principally of aluminum ions (Table 4 and 5).

Analysis of results: Behavior against corrosion of industrial aluminum alloys has been extensively studied in relation to their application areas (transport, energy, civil engineering, etc.), but also in the context of basic research. These studies, however, are much less numerous in the food area of concern. Moreover, in this case, the work focus on the food brought into contact with the materials from which it attempts to value the mass transfer. The authors usually do not treat the degradation of the material itself seen through the concepts of materials science, so that linking two aspects of the problem is quite innovative.

Corrosion of aluminum: The aqueous corrosion has been widely studied because a large part responsible for

the degradation of materials. It starts, for aluminum and its alloys, by the attack of the protective film of alumina (Al_2O_3) that covers these spontaneously materials exposed to the open air (Vargel, 1979).

For the pure aluminum, layer is continuous and even tends to thicken when the latter is immersed in boiling water. This is the boehmitage, an operation performed to treat superficially industrial aluminum (formation of boehmite, $Al_2O_3 \cdot H_2O$). In the presence of Cl^- ions, which are found for example in tap water, less than $200 \mu g/L$ (Decree No. 2001-1220 of 20-12-2001), on the basis of our corrosive solutions, this protective layer may locally disappear (Ergun *et al.*, 1997), placing the bare aluminum that becomes an anode.

This produces an aqueous and pitting corrosion as described by Vargel (1979) in his work on the behavior of aluminum and its alloys. This mechanism is governed by the concentration of H^+ ions in the solution, that is to say, its pH and the electrical potential E of the workpiece relative to the solution (Landolt, 2003).

Corrosion of aluminum alloys handcrafted: In our aluminum alloys, the microstructure is formed from a

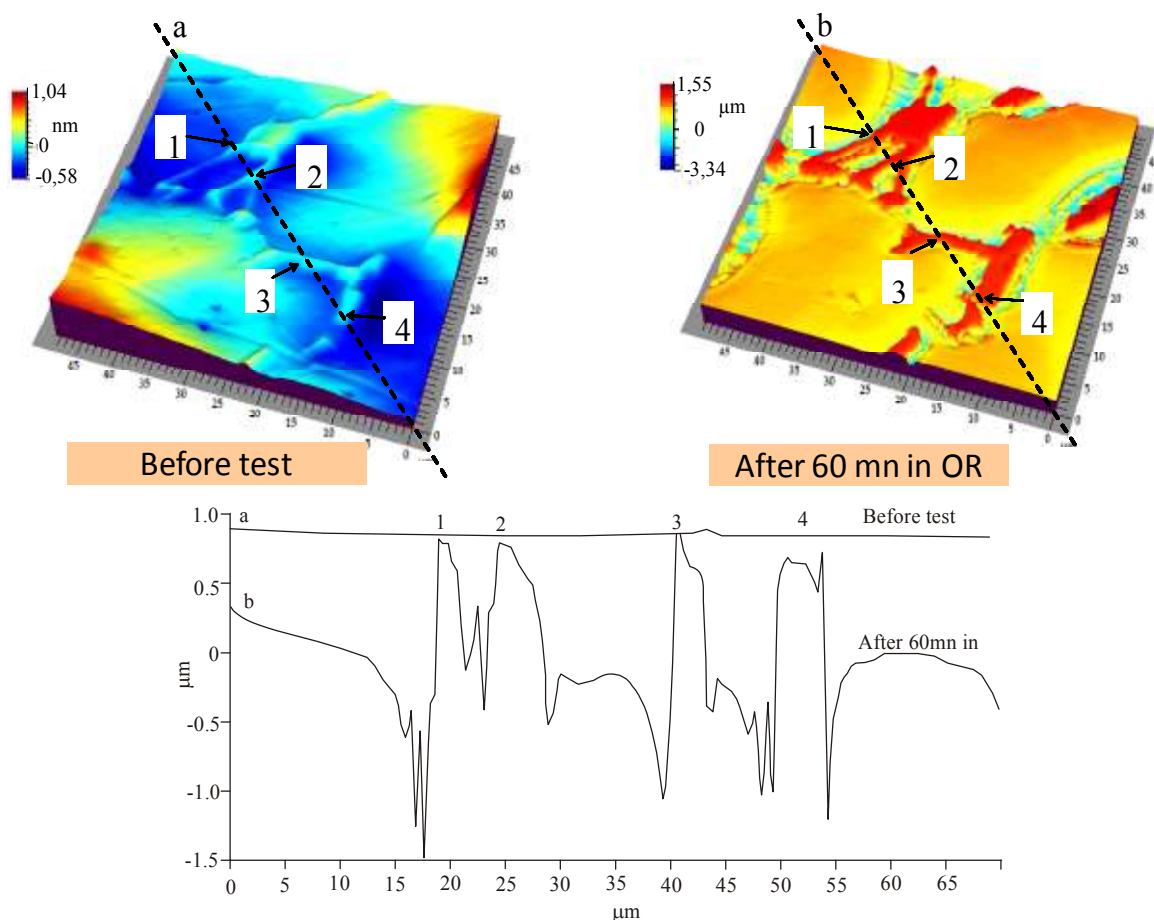


Fig. 3: Micrography Ech 03 before and after test in OR

mixture of phases (Ndiaye *et al.*, 2012), including a majority of primary aluminum crystals and intermetallic compounds of silicon. Different phases with various corrosion potential (Wei *et al.*, 1998; Pao *et al.*, 2001), a galvanic coupling is established between the various components of the structure and anodic areas pass into solution.

Degradation of the material is then manifested by the appearance and development of pitting on the aluminum matrix. Intermetallic compounds and silicon are located at the grain boundaries of crystals of primary aluminum, is called "intergranular corrosion" (Wei *et al.*, 1998; Pao *et al.*, 2001), which can be activated by the presence of Cl⁻ions. We can observe to the following micrographs (Fig. 3 and 4) intergranular corrosion Ech 03 after corrosion in the OR environment. Just below we overlay the roughness profile before and after the test (Fig. 3). Figure 4 also shows the effects of corrosion observed Ech 01 by AFM.

Thus we see that the aluminum corrodes preferentially to silicon intermetallic compounds and confirm, from this point of view, the mechanism of corrosion by galvanic coupling in an aqueous medium of different phases present in the industrial aluminum alloys observed by different authors (Wei *et al.*, 1998;

Pao *et al.*, 2001; Fractila-Apachitei *et al.*, 2006; Andreatta *et al.*, 2004).

However, other authors (Guillaumin and Mankowski, 2000) noted the different behavior of Mg-rich precipitates which anodic relative to aluminum, are dissolved. Magnesium is associated with zinc compounds MgZn₂ type these two elements will therefore go into solution in the food industry.

Thus, in all scenarios, the attack of the aluminum-silicon interface or intermetallic aluminum compounds will lead to a loosening of the latter, which will be incorporated into foods in their solid form.

From the above analysis we can conclude that the study of the corrosion of metals by food media becomes complicated because of the wide variety of chemical species they contain, species varies according to the origin of the product, mode preparation and cooking of the food. It is therefore very difficult to control all of these factors to have a stable and reproducible environment in tests and compare the test results with those obtained by other authors.

The roughness parameter R_q measured gross polishing surface (initial state), of the order of tens of nanometers, in the passes after corrosion OR solution at a value of about several hundred nanometers. But in TF and CT solutions there are no major changes in R_q.

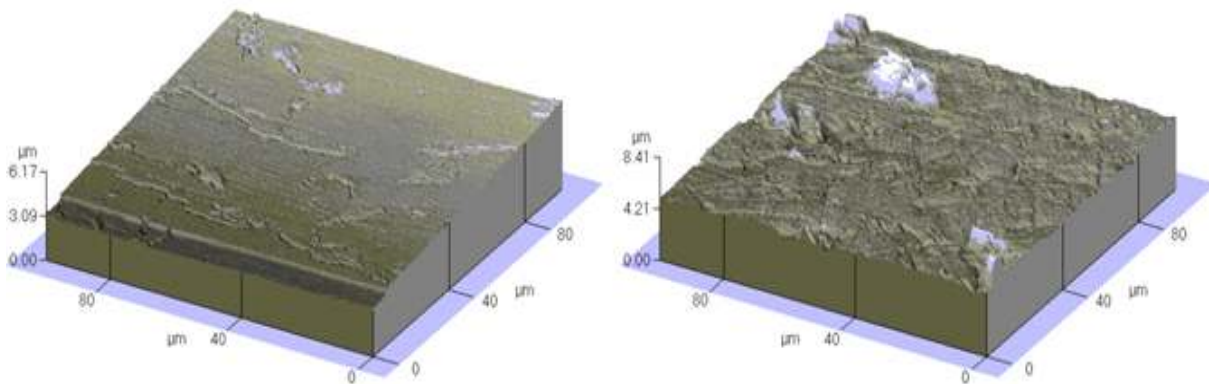


Fig. 4: Ech01 before and after 30 mn test in OR (AFM)

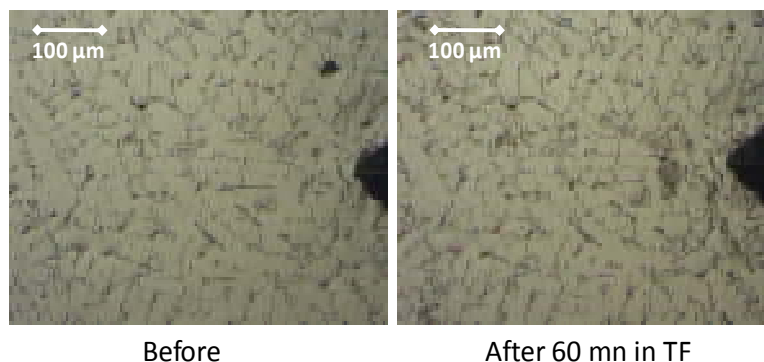


Fig. 5: Ech 03 before and after test in TF

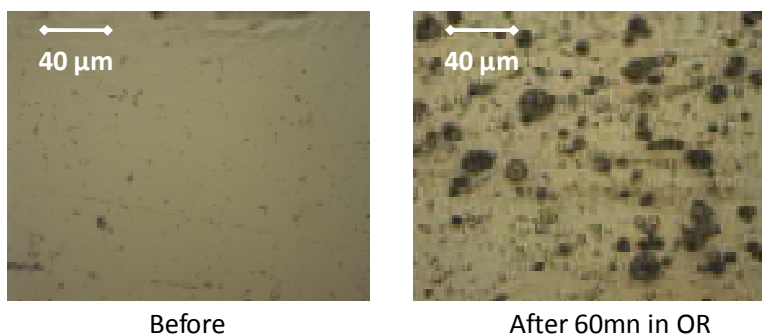


Fig. 6: Pittings on alupur before and after test in OR

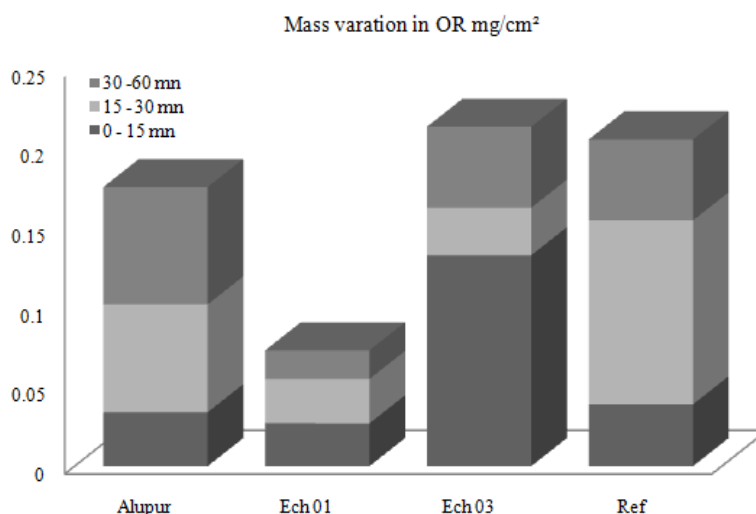


Fig. 7: Mass variation in OR

This is corroborated by observations strongly microscope as shown in Fig. 5.

The tomato fruit is naturally acid, then experience with tomato takes place in an acid medium with a pH around 4.7.

Pitting corrosion is a mechanism that can be activated by, among other pH as has been presented by several authors (Zaid *et al.*, 2008). In our experience, our protocol did not allow us to demonstrate this result. However we intend to correct in future research.

Mass loss of samples: Changes in mass loss are barely detectable for CT environments and TF but significant for OR environment. For this latter medium, they have the same general shape showing a first stage (0 to 30 min) during which the mass loss is fast, then a second stage where the development of the variation of the weight function time is much lower (Table 6).

This high rate of weight loss at the beginning of the test is mainly due to detachment of some of the solid particles unpolished surface of the samples, from the casting operation and not removed by the cleaning operations (finishes), but also to pitting whose development is fairly rapid test result in early containment of corrosion products: pitting by

Table 6: Mass variation speed in mg/cm².h

Mass variation in OR mg/cm ² .h	Alupur	Ech 01	Ech 03	Ref
0-15 mn	0.13±0.02	0.11±0.02	0.13±0.02	0.15±0.02
15-30 mn	0.27±0.02	0.10±0.02	0.12±0.02	0.46±0.02
30-60 mn	0.29±0.02	0.07±0.02	0.20±0.02	0.20±0.02

electrolytic potential difference (Vargel, 1979). The corrosion rate of pure aluminum proves that pitting corrosion is equally important that the intergranular corrosion observed in Fig. 3 and 4. Figure 6 shows and pitting observed on pure aluminum corrosion after an hour in the OR environment.

It also appears that the weight loss of Ech 03 is greater during the first quarter as shown in the Fig. 7.

This may be partly explained by the chemical composition and microstructure of Ech 03.

We also observe that Ech 01 has a total mass loss quite low compared to other samples. At the current state of the study, we believe that this could be related to the microstructure. We plan to initiate further research in this direction.

The transfer of ions to the substrates: The results show a significant presence of aluminum ions in the

substrate with the rice. This is also explained by the principle of receding intermetallic presented with the results of the micrograph.

Rice is a cereal consumed daily, the presence of ions poses the problem of the toxicity of substrates with respect to man. This study should be conducted in collaboration with specialized medical departments.

We also note the presence of chloride ions in the solution CT, intentionally introduced in the preparation of tomato paste to increase its shelf life. However, while these ions promote degradation of the natural protective layer of alumina Al_2O_3 , (Ergun *et al.*, 1997; Vargel, 1979), there is no significant corrosion of the samples. According to some authors (Zaid *et al.*, 2008; Ndiaye *et al.*, 2012), these levels of chloride ions seem low to allow a significant degradation of the natural protective layer of aluminum and thus promote corrosion.

CONCLUSION

Recycled handmade aluminum alloys in Senegal do not respond to standard NF EN 601. The experiences we have just completed shows that degradation is significant in water with rice. The observed is an intergranular corrosion mechanism which preferentially attacks the aluminum grains around the intermetallic combined with pitting. In the end, so we have a loosening of these grains that eventually reach the substrate. This mechanism explains the loss of weight during the test and the presence of aluminum ions at varying levels in the substrates. It would be interesting to see the effect of the ingestion of these substrates on human health. This study could be conducted by a team comprising interdisciplinaire medicine specialists.

We also note that the mass loss depends on the chemical composition and the microstructure is much more pronounced in the OR environment. A study on the impact of the microstructure in the mass loss would lead to interesting. Expected results may help to propose solutions to minimize the transfer of metal ions into the substrate when using utensils recycled aluminum alloys.

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