

Stress Corrosion Cracking of Cast 6063 and Deep Drawn 1017 Aluminum Utensils In *Lycopersicum esculentum*

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(Submitted February 17, 2006)

In the black world cup-shaped utensils cast or deep drawn are usually used for cooking purpose. The utensils are made from deep drawn aluminum alloy of the 1xxx series and for cast 6xxx series. The cylindrical shape utensil is subjected to domestic heating cycles and after a while, tiny hole-like features termed pits will appear. This development will eventually shorten the service life of aluminum cooking utensils. This article examines the chemical response of deep drawn and cast utensils made from 1017 and 6063 aluminum alloys, respectively, in solution of *Lycopersicum esculentum* at a temperature other than ambient temperature. The results show that cast cylindrical utensils pit much more readily than deep drawn utensils. This occurrence is traceable to the presence of microcracks as a result of hydrogen embrittlement phase, precipitation of brittle second phase particles and the fine texture in cast utensils. The aluminum alloy can fail by cracking along grain boundaries when exposed to specific environments.

Keywords aluminum alloy-corrosion-cracking, deep drawn, *Lycopersium esculentum*, stress, workhardening

Nomenclature

wc	cast sample wall
wd	deep drawn sample wall
bc	cast sample base
bd	deep drawn sample base
cc	cast sample corner
cd	deep drawn sample corner
C_W^C	Corrosion rate of the wall of the cast sample
C_W^D	Corrosion rate of deep drawn sample wall
C_B^C	Corrosion rate of cast sample base
C_B^D	Corrosion rate of deep drawn sample base
C_C^C	Corrosion rate of cast sample corner
C_C^D	Corrosion rate of deep drawn sample corner

1. Introduction

One well known property of aluminum is its lightweight. It can be formed by processes in use today, and through alloying, it can attain strengths twice that of mild steel. Despite the introduction of polymers and composites in recent years, aluminum alloy remains important in structures, because of its weight to strength ratio, stiffness, and toughness. It is resistant to corrosion by natural atmospheres and by many foods and chemicals. The best combination of strength and corrosion resistance for consumer applications in wrought products is found among the 5xxx and 6xxx series alloys. However, the 1100 series are also being used. It has been reported (Ref 1) that several casting alloys have good corrosion resistance, and

aluminum castings are widely used as cooking utensils and components of food processing equipment.

Corrosive attacks on aluminum alloy products often result to pitting, which generally occurs in a pH range of about 4.5-9.0, where the oxide film formed is usually unstable. The concentration and size of the pits often depend on alloy composition, oxide film quality, and the nature of the corroding environment.

Surface film provides mechanical barriers, which limit the transport of the aggressive ions while the film, may act to entrain the reaction occurring within the developing pit (Ref 2, 3).

Study on corrosion of aluminum in fresh water has shown that oxygen ion, chloride ion, and carbonate ion were necessary for deep pitting but higher-chloride contents result in more general pitting (Ref 3, 4). In the temperature regime of 100 °C, the reaction between aluminum and water gave the major products as boehmite, which forms on aluminum surface at higher temperature. The stoichiometry of this consists $Al(OH)$ and $Al(OH)_3$.

This article studies the corrosion response of cast and deep drawn utensils in *L. esculentum* (tomato) solution.

Lycopersicum esculentum is of the Solanaceae family. It contains citric, oxalic, and malic acids. There are microforms of bacteria and macro types such as algae and fungi, which may cause metal deterioration. These microorganisms have been observed to live and reproduce in media with pH values between 0 and 11 and within a temperature range of 17-100 °C and similarly under pressure.

Living organisms sustenance through chemical reactions involving ingest food and waste products elimination can affect corrosion behavior by influencing anodic and cathodic reactions, protective surface films formation or destruction, creating corrosive conditions, and producing deposits.

2. Experimental Methodology

Aluminum 6063 scrap obtained from NIGALEX (Nigerian Aluminum Extrusion Limited, Oshodi) was cast into a cylindrical cup (utensils), while a deep drawn cup (utensil) produced

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by Tower Aluminum for the test was obtained from the local market. The chemical compositions of the test samples are shown in Table 1.

2.1 Sample Preparation

Cast and deep drawn utensil with their respective dimension 10 mm×10 mm×5 mm and 10 mm×10 mm×2 mm were prepared for test from the base, corner and wall. The samples were labeled, dressed, and weighed are subjected to *Lycopersicum* fruits solutions, placed in corked conical flask. Using Jenway 350 meter the pH of the solution (6.19) was recorded.

Each *Lycopersicum* solution contains six samples of either cast or deep drawn utensils with two each gotten from the base, corner and wall.

Samples with dimension 10 mm×10 mm×5 mm were obtained from the base, corner and wall of the cast utensil. From the deep drawn utensil, samples of 10 mm×10 mm×2 mm were prepared for test from the base, corner and wall.

The samples were subjected to three different tests, which involve:

- Heating the samples for 20 min, cooling at 30 °C and super cooling at 4 °C.
- Heating the samples for 20 min, cooling at 30 °C without super cooling at 4 °C.
- Control test at room temperature (30 °C).

Weighing of samples was done after 3 days of immersion using Mettler Toledo AB 204 weighing machine. The solutions were renewed after sample weighing. At the end of the tests, one surface of each sample was prepared for metallographic examination, using a mixture of nitric acid, hydrofluoric acid, and water as etchant for about 50 s. The micrographs obtained are shown in plates 1-6.

3. Results and Discussion

Corrosion rates were evaluated and the results tabulated in Tables (2-4).

The corrosion rate of test-piece cut from the base of the deep drawn cup is more than 1.5 times higher than that at the cup

Table 1 Spectrometer analysis of test samples in percentage

Composition	Al	Si	Fe	Cu	Mn	Mg	Zn	Cr	Ti	Ca	Se
Cast utensil	98.73	0.44	0.20	0.0117	0.0131	0.5711	0.0060	0.0027	0.0080	0.0033	-0.0003
Deep drawn utensil	99.37	0.17	0.43	0.0012	0.0088	0.0047	0.0041	0.0013	0.0120	0.0008	0.0001

Table 2 Corrosion rate of cast and deep drawn samples heat treated with super cooling in *L. esculentum*

Time, h	Weight loss, mg		Corrosion rate, Mils/year×10 ³		Weight loss, mg		Corrosion rate, Mils/year×10 ³		Weight loss, mg		Corrosion rate, Mils/year×10 ³	
	<i>wc</i>	<i>wd</i>	<i>C_w^C</i>	<i>C_w^D</i>	<i>bc</i>	<i>bd</i>	<i>C_B^C</i>	<i>C_B^D</i>	<i>cc</i>	<i>cd</i>	<i>C_C^C</i>	<i>C_C^D</i>
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00	0.00	0.00	0.00
72	0.00	0.00	0.00	0.00	0.00	0.2	0.00	1.27	0.00	0.80	0.00	5.09
144	0.20	5.00	0.44	20.14	0.10	1.2	0.22	3.79	0.40	1.60	0.89	5.09
216	3.70	9.00	5.46	24.17	6.10	3.9	9.00	8.22	2.10	9.5	3.10	20.19
288	6.70	15.00	7.42	30.20	16.70	15.4	18.49	24.37	8.90	25.8	9.85	41.11
360	16.40	16.90	14.53	27.23	25.20	31.0	22.33	39.25	22.5	26.8	19.94	34.17
432	20.60	18.70	15.21	25.11	28.0	41.0	20.68	43.26	28.8	30.2	21.26	32.08
504	21.60	21.10	13.67	24.28	38.6	45.2	24.43	40.88	29.70	32.9	18.99	29.96
576	23.30	26.30	12.90	26.48	41.9	54.0	23.20	42.73	33.50	33.8	18.55	26.93
648	27.00	27.30	13.29	24.43	57.0	82.0	28.06	57.68	35.4	39.4	17.43	27.90

Table 3 Corrosion rate of cast and deep drawn samples heat treated without super cooling in *L. esculentum*

Time, h	Weight loss, mg		Corrosion rate, Mils/year×10 ³		Weight loss, mg		Corrosion rate, Mils/year×10 ³		Weight loss, mg		Corrosion rate, Mils/year×10 ³	
	<i>wc</i>	<i>wd</i>	<i>C_w^C</i>	<i>C_w^D</i>	<i>bc</i>	<i>bd</i>	<i>C_B^C</i>	<i>C_B^D</i>	<i>cc</i>	<i>cd</i>	<i>C_C^C</i>	<i>C_C^D</i>
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
72	0.00	0.00	0.00	0.00	0.60	0.00	2.66	0.00	0.20	0.00	0.88	0.00
144	2.9	0.10	6.43	0.40	4.60	1.1	10.19	3.48	20.4	0.70	45.19	2.23
216	5.0	0.20	7.38	0.53	6.40	2.2	9.45	4.64	20.6	11.0	30.42	23.37
288	10.4	2.9	11.52	5.84	10.6	3.6	11.74	5.69	23.5	12.1	26.03	19.28
360	11.2	4.1	9.92	6.61	13.1	4.0	11.60	5.06	23.6	14.5	20.91	18.49
432	12.8	4.2	9.45	5.63	13.8	8.4	10.19	8.86	27.5	17.8	20.30	18.91
504	13.8	6.7	8.73	7.71	15.1	9.2	9.56	8.32	27.7	18.4	17.53	16.76
576	15.3	7.4	8.47	7.45	16.3	9.3	9.02	7.36	28.7	18.7	15.89	14.90
648	15.7	7.6	7.73	6.80	17.4	26.2	8.57	18.43	39.8	19.1	19.60	13.53

Table 4 Corrosion rate of cast and deep drawn samples unheated and without super cooling in *L. esculentum*

Time, h	Weight loss, mg		Corrosion rate, Mils/year $\times 10^3$		Weight loss, mg		Corrosion rate, Mils/year $\times 10^3$		Weight loss, mg		Corrosion rate, Mils/year $\times 10^3$	
	<i>wc</i>	<i>wd</i>	C_W^C	C_W^D	<i>bc</i>	<i>bd</i>	C_B^C	C_B^D	<i>cc</i>	<i>cd</i>	C_C^C	C_C^D
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
72	0.2	1.20	0.89	9.67	0.60	0.00	0.26	0.00	0.00	0.30	0.00	1.91
144	2.0	1.60	4.43	6.44	0.90	0.20	1.99	0.63	4.60	1.60	10.19	5.10
216	3.3	1.80	4.87	4.83	2.3	0.40	3.39	0.84	5.20	7.80	7.67	16.57
288	3.5	2.00	3.87	4.02	2.3	1.90	2.55	3.00	6.60	8.00	7.31	12.70
360	3.8	2.10	3.37	3.38	2.7	2.10	2.39	2.65	8.50	8.10	7.53	10.33
432	6.8	2.10	5.02	2.82	3.0	2.60	2.22	2.74	9.70	8.20	7.16	8.71
504	7.7	2.60	4.87	2.99	3.2	2.8	2.03	2.53	10.30	8.30	6.52	7.56
576	9.5	3.50	5.26	3.52	6.5	3.0	3.60	2.37	10.90	8.50	6.04	6.77
648	26.6	4.0	13.09	3.58	23.0	3.8	11.32	2.67	11.3	9.60	5.56	6.79

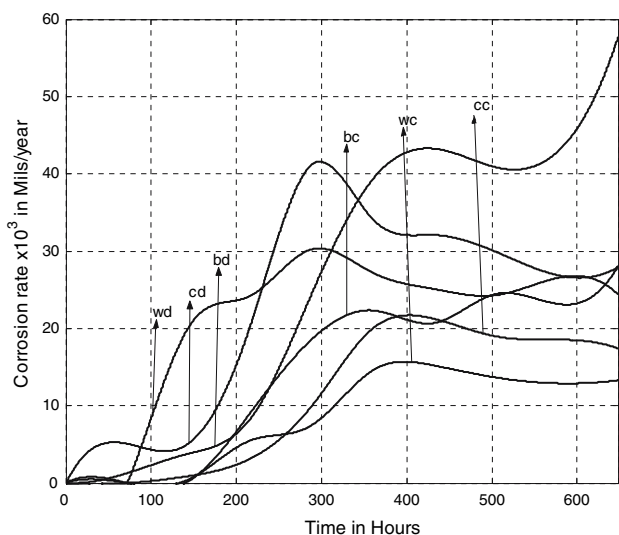


Fig. 1 Corrosion rates of heat treated and super cooled utensils

wall and curvature (Table 2 and Fig. 1). The pattern of corrosion rate in the various sections is observed as $bd > cd > wd$. During deep drawing, a form of crevice corrosion can occur, whereby the grain boundary corrodes with the specimen surface and the crack walls remaining passive. This gives rise to intergranular corrosion, which may be distributed over the specimen when stress is applied, since the latter will simply open up the cracks. During annealing after forming, there appear very few nuclei at the corner due to the small cold deformation that has taken place there. Consequently, the grain at corner may be coarse. At the wall, the grain is fine due to recrystallization process as a result of the amount of workhardening. Thus the base and wall consist of very fine-grain structure, which is more susceptible to corrosion.

If the cup is subjected to heating cycles in domestic kitchen while containing a solution with pH 6.19, the base will respond to anodic reaction more than the wall and corner as a result of the fine-grained structure and the direct thermal stresses. The boundary between the base and corner, and wall and corner will be more susceptible as a result of the existence side by side of fine and coarse grains. Thus pits, which are the failure characteristic of deep drawn cup could be seen at the base and at the interface where there is transition from fine to coarse

grain structure or vice versa. During heating cycles, the corner that is relatively lower in thickness compared to base rapidly conducts heat away. Heat conduction is restricted through the base since the latter is adjacent to the heat source. The wall on the other hand is quite distant from the heat source and may not be restricted in the process of heat conduction. Thus the thermal-assisted natural aging has little effect in this region. This phenomenon, however, increases the hardness of the base significantly thereby increasing the rate of anodic reaction in the base under the observed environment. Perhaps, if the heating is equally carried out simultaneously from both *x*-, *y*-, and *z*-directions, its effect due to differential heating and restriction could be eliminated.

The observed corrosion rate in a cast cup also shows the same trend as in deep drawn cup i.e. $bc > cc > wc$. In a cast cup, the base usually will consist of chilled crystals, as there is no restriction to the outward flow of heat. The immediate environment after the mould is air. The wall will consist of equiaxed crystals due to slow cooling as a result of restriction to the cup platform. The crystals are thus large, soft, and relatively stress free. The corner is a region between the base and wall and will consist of a mixture of columnar, chilled, and equiaxed crystals. There is also the likelihood of internal cavities left by air bubbles developed in the region as a result of sharp or sudden change in path of metal profile configuration. The chilled-crystals are hard and significantly stressed and it will promote corrosion in an aggressive environment. This may account for the high-corrosion rate observed. The corner having a relatively high-corrosion rate could be attributed to a tripartite action of the former and the presence of microcracks and texture. Thus the corrosion rate lies between the lowest and the highest. The development of microcracks at the corner region seems to agree with Griffith theory of brittle fracture that a brittle material contains a population of fine cracks. The cracks produce a stress concentration of sufficient magnitude. When any of the cracks spreads to a brittle fracture, it produces an increase in the surface area of the size of the crack, which requires an increase in the surface energy (Ref 5). The source of the increase surface energy is the elastic strain energy which is released as the crack spread.

The corrosion rate of test pieces of cast cup (6063) is higher than that of deep drawn cup (1017) as shown in Fig. 1-3. The reason for this result has to do with texture, the presence of microcracks and the nature of the second phase particles. The cast cup consists of greater percentage of highly stressed fine

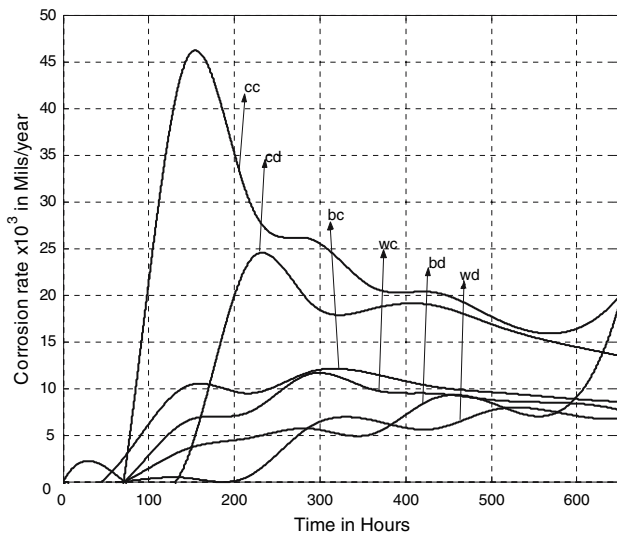


Fig. 2 Corrosion rates of heat treated utensils without super cooling

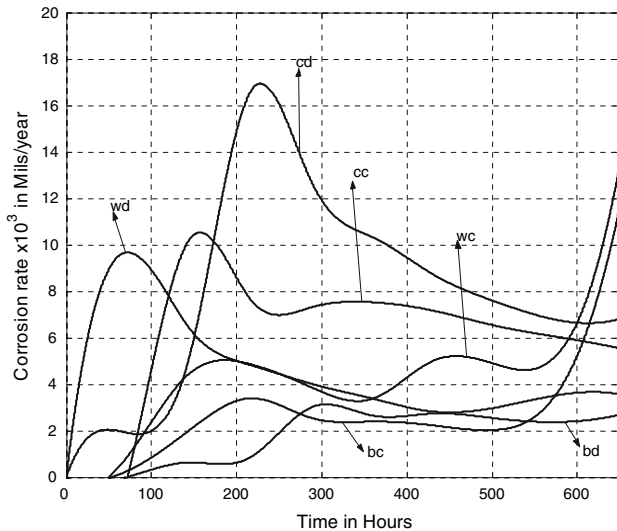


Fig. 3 Corrosion rates of non-heat treated utensils without super cooling

grains, the presence of microcracks and the precipitation of magnesium-based second phase particles which accelerate the corrosion propensity in the regions over that observed in deep drawn cup. It should be noted that in castings, annealing does not significantly alter the microstructure, as is the case with deep drawn cup (Ref 6).

Heating and super cooling of cast and deep drawn pieces in aggressive environment will promote pitting corrosion. For deep drawn piece corrosion rate will be retarded if the piece is super cooled after heating. Conversely, the corrosion rate in cast piece will either decrease or increase depending on the amount of discontinuities resulting from variation in texture toward the curvature.

Cast piece anodic reaction in this environment decreases when neither heating nor super cooling is done. This, however, promotes anodic reaction in deep drawn piece. The corrosion rate of cast test piece at the wall is higher than the other two sections when heated and super cooled in the test medium. But when both the test pieces and test medium are heated and left at room temperature, the curvature test piece corroded faster. Test pieces in test medium examined at room temperature shows the base test piece corroding faster than the other sections.

The corrosion rate of test piece in medium subjected to heating and super cooling gave the highest value at the wall of the deep drawn cup. But the base corroded slightly more than the curvature and wall when the system is heated and not cooled (Fig. 3). However, there is a significant increase in this behavior for systems examined at room temperature.

The as-cast structures of wall test piece indicate precipitations of large spheroid particles of Mg_2Si the second phase in a matrix of equiaxed crystals of aluminum. Similarly, blowholes are visible (plate 1A). This second phase particles were largely eroded as can be seen in (plate 1B). The as-cast structure of base test piece revealed large amount of finely dispersed spheroid Mg_2Si particles in the aluminum matrix, which indicates high rate of cooling taken place in this section (plate 2A). The Mg_2Si particles were heavily eroded in an intergranular manner, leaving behind discontinuous grain boundaries of the main matrix (plate 2B). The as-cast curvature test piece contained substantial amount of finely dispersed spheroid particles of the Mg_2Si in a matrix of aluminum (plate 3A). The second phase particles were however eroded but not as much as in the base test piece (plate 3B).

For the deep drawn wall test piece, there are large amount of finely dispersed spheroid particles of $FeAl_3$ as second phase in the aluminum matrix (plate 4A). Some of these particles were eroded during the test (plate 4B). The base test

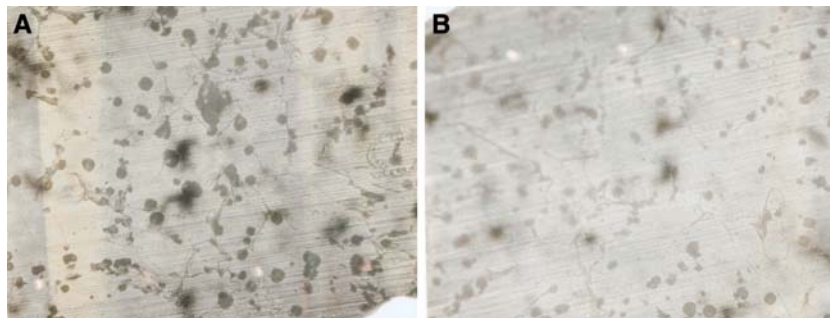


Plate 1 A and B. Wall (side) section of cast utensils

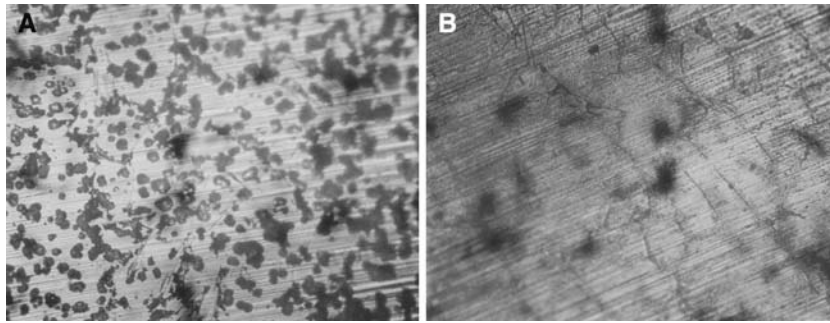


Plate 2 A and B. Bottom (side) section of cast utensils

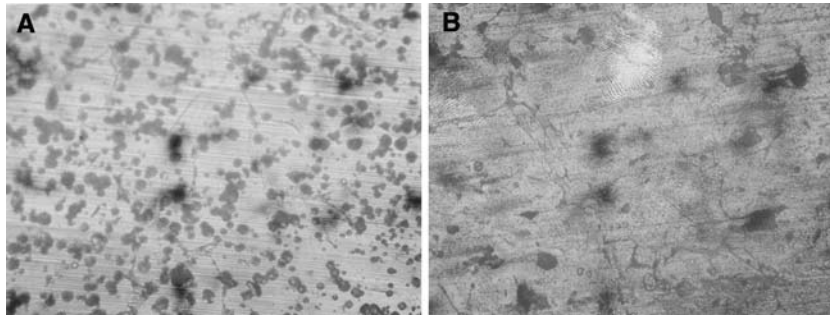


Plate 3 A and B. Corner (side) section of cast utensils

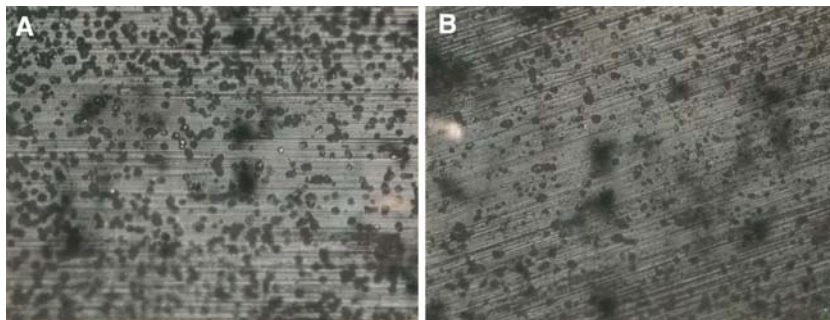


Plate 4 A and B. Wall (side) section of deep drawn utensils

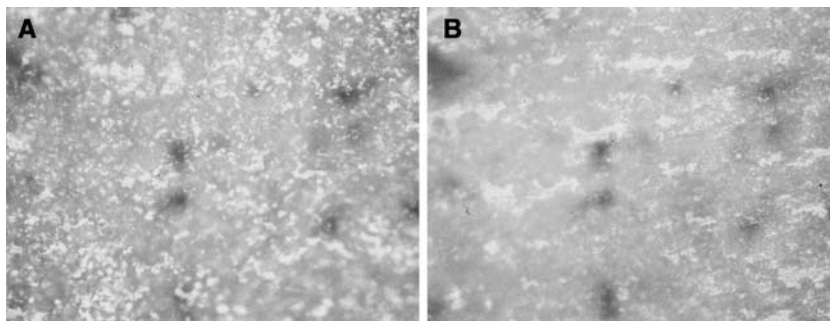


Plate 5 A and B. Bottom (side) section of deep drawn utensils

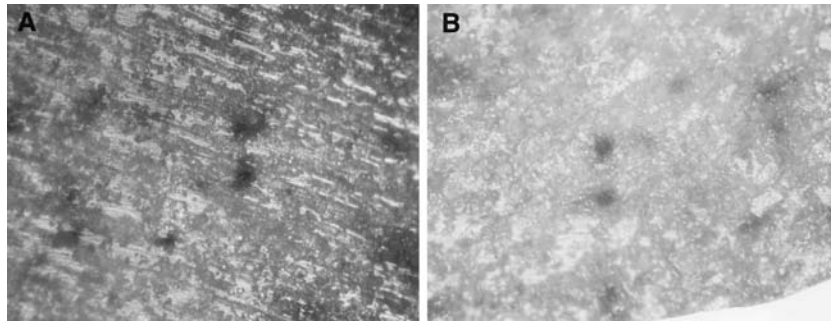


Plate 6 A and B. Corner (side) section of deep drawn utensils (A: Control samples (not heat treated and no super cooling) B: Heat treated without super cooling)

piece revealed greater population of very fine FeAl_3 particles in the aluminum matrix, which were alternately positioned in the aluminum matrix (plate 5A). Much of this phase remains during the test period (plate 5B). The curvature test piece revealed an elongated fine structure of the FeAl_3 in the (direction of rolling) aluminum matrix (plate 6A). Some of these were washed off during the test as seen in (plate 6B).

4. Conclusion

This work has shown that there is an insidious form of corrosion in both 6063 and 1017 aluminum alloys with a marked loss of mechanical strength and little mass loss. It revealed that the presence of microcracks, fine texture and the precipitation of brittle second phase particles in cast cup will weaken the corrosion resistance of 6063 aluminum alloy over that of deep drawn cup of 1017 aluminum alloy. The deformation of aluminum 1017 alloy and its subsequent annealing help to improve its corrosion resistance in 'L. esculentum' solution during domestic heating cycles. There is the tendency of hydrogen embrittlement in the aluminum alloys, even though the FCC microstructure means that the transport of hydrogen is slower than in high strength steels, and hence the crack growth rate may be lower. The cracking here is intergranular. The susceptibility becomes more severe as the strength of the alloy is increased and environment

(solution of *Lycopersicum*) provides hydrogen. This inclusion and other impurities in melt are not uniformly distributed, as is the case for a workhardening profile. The assertion that a good gate design is independent of the cast and the gate design rules could be used in order to minimize the agitation and avoid erosion of the sand mould by metal stream. This is done through orienting the gates in the direction of the natural flow paths. The use of multiple gating to lower pouring temperatures and thereby improving the metallurgical structure of casting is desirable.

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