Embrittlement of ADI by contact with liquids: influence of alloy content and preventive methods

R. E. Boeri and R. A. Martínez

In view of its excellent mechanical properties and low cost when compared to high strength steels, austempered ductile iron (ADI) is being applied to replace mechanical components in different applications. However, ADI is known to suffer noticeable embrittlement when its surface is in contact with liquids during quasi-static tensile testing. Although the embrittlement phenomena has been characterised in detail, the acting mechanism is not well understood at the present time. Water has shown to cause the greatest degree of embrittlement, while other liquids, such as alcohol and other organic reagents, cause milder though noticeable effects, too. An apparently obvious protection of ADI against the embrittlement caused by liquid environments would be through ADI surface isolation from the environment. The present article examines the efficiency of several paints and coatings by means of tensile tests carried out under dry and wet conditions. From a good number of protective coatings applied on the tensile samples, only one was able to protect the sample under stress from water contact, thus preventing the embrittlement phenomena. The protection method is effective when the layer integrity is not affected by the deformation undergone by the substrate. Another aspect dealt with in the present paper is the assessment of the influence of the chemical composition on the susceptibility of ADI to embrittlement. The results show that the presence of alloy elements in the melt does not influence the degree of embrittlement in the samples.

Keywords: ADI, Water, Embrittlement, Alloy, Protection, Fracture

Introduction

Ductile iron (DI) is a family of cast alloys that covers a wide range of mechanical properties, depending on their matrix microstructure. Ferritic matrixes are used in parts, such as automotive suspension components, where a high impact property is the main requirement. On the other hand, pearlitic and martensitic matrixes are used when hardness, strength and wear resistance represent a major issue.

Ductile iron has been employed to replace cast and forged steels in a large number of applications, and its production has maintained a sustained rate of growth over the last decades. Currently, researchers and producers are developing new applications for DI and target the market of safety critical parts requiring the combination of strength and toughness on a regular basis.

The strength of nodular graphite DI is increased after an austempering heat treatment process, obtaining the so called austempered DI (ADI). The microstructure of the resulting matrix is a combination of acicular ferrite and high carbon austenite, also known as ausferrite.

However, ADI suffers noticeable embrittlement when its surface is in contact with liquids during slow monotonic tensile load applications.[1–7] Water has shown to cause the greatest degree of embrittlement, while other liquids, such as alcohol and other organic reagents, cause milder though noticeable effects, too. The origin of embrittlement remains to be thoroughly explained. Nevertheless, this relatively unusual effect has not stopped the increasing application of ADI in the construction of high strength mechanical components. In fact, reports of ADI part failure as a result of embrittlement caused by water or other liquids are very atypical. The very low incidence of brittle failure of ADI in service is probably explained by two unique characteristics of this effect: it is fully reverted after the part surface is dried, and it is unnoticed at high loading rates. As a result, failure in service requires a relatively slow overloading when the part is in contact with liquids, which does not occur very frequently.

The first reports of embrittlement by contact with water were published by Komatsu *et al.* and Shibutani *et al.*[1,2] Martínez *et al.*[3] verified the existence of the phenomenon when obtaining similar results after testing

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several ADI grades (ASTM A807M-06). Such studies showed that reductions in tensile strength and elongation can yield values of 30 and 70% respectively. Embrittlement is not dependent on water pH for an interval of 5·5–11·9.[3] Some researchers have proposed that this phenomenon is caused by hydrogen,[1] but this hypothesis was refuted after the surface of tensile tests were exposed to controlled electrochemical potential, inhibiting or promoting proton generation at the surface.[10] This conclusion was confirmed by Caballero *et al.*[11]

The stress required for a sharp crack or a flaw to propagate in a sample surrounded by liquid is lower than that necessary in dry conditions. The velocity of the crack or fracture propagation has been estimated to be 10–100 cm s^{-1}.

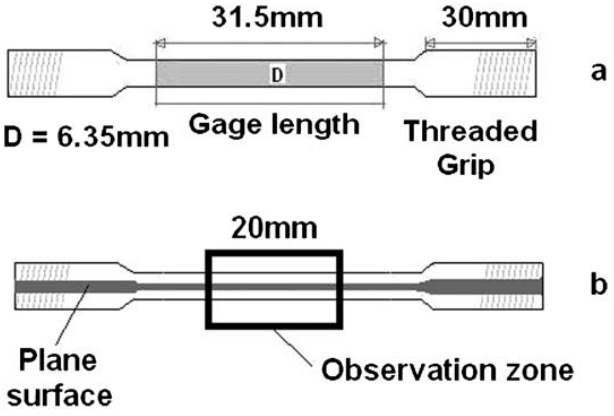
Despite the apparent lack of practical incidence of the embrittlement effect, the identification of technical means to alleviate its influence is highly desirable. A first look into the problem would indicate the convenience of painting or coating the surface of ADI parts to isolate it from the environment.

Another aspect worth considering when it comes to analyzing the mechanical properties of DI is its associated solidification process, which starts with graphite and austenite nucleating independently into liquid, with the austenite growing dendritically. The austenite dendrites trap the surrounding nodules as the solidification process advances. Carbon diffusion to the nodules makes them grow by diffusion in solid state. As a result of this process, one dendrite contains several nodules. Then, the dendrites and nodules grow together, leaving isolated liquid zones among them that solidify at the end of the process. These zones between dendrites are known as the last to freeze (LTF) zones. Given the fact that LTF zones solidify at the end of the process, they can show a higher concentration of some alloy elements and impurities as well as small shrinkage cavities.[6,7]

The chemical composition of DI always includes Mg, C, Mn, Si, S and P, while elements like Mo, Cu and Ni are frequently found as alloying elements. The concentration of the second group of elements in the metallic matrix is not homogeneous, giving a characteristic known as segregation. When this feature is present in a range of approximately hundreds of micrometres, it is called microsegergation. Yet, if this range becomes greater, it is referred to as macrosegregation. The latter can be effectively controlled, but microsegregation cannot be avoided; it always occurs.

Hence, the ADI fracture process should be analysed on a material with hollow spherical bubbles of different sizes (the strength of the graphite occupying these sites is negligible), taking into account the ausferritic metallic matrix and certain sites in the matrix (LTFs) where microporosity, cast defects, non-metallic inclusions (sand from moulds) retained austenite and carbides may be present.

Indeed, these zones present adverse characteristics from a mechanical property viewpoint. Since LTF zones are the main spot for crack initiation when the material is loaded, and these cracks have been identified as the first stage of the embrittlement process, the objective of the present work is to assess the influence of minimising the thickness of the LTF zones by comparing the embrittlement of ADI alloys showing cleaner or less deleterious LTFs with those of alloyed melts.



1 Samples used in mechanical tests

Regarding the scenario described above, the goal is to examine the ability of several paints and coatings to protect ADI from the embrittlement phenomenon as well as the effect of using very low alloyed melt to test, under wet conditions, the embrittlement of a material with supposedly less detrimental LTF zones.

Experimental

Two ductile cast iron melts were prepared in a medium frequency induction furnace. Steel scrap and foundry returns were used as raw materials. Nodulisation was carried out using the sandwich method with 1·5 wt-%Fe–Si–Mg (6%Mg). The melt was inoculated with 0·6 wt-%Fe–Si (75%Si). The chemical composition of the melt was determined using a Baird DV6 spectrometer. One inch 'Y' blocks were cast in sand moulds. Round bars of 12 mm diameter were cut from the Y blocks and used to prepare metallographic and mechanical test samples.

The chemical compositions of the melts used are listed in Table 1. The DI in cast A has a near eutectic composition and includes small amounts of Cu and Ni, which were added to increase austemperability. Melt NA, in turn, does not include any of these alloy elements in its composition. The samples of both melts yielded a very similar nodule count of 120 nodules/mm^2, nodule size of 5 and a nodularity of 100%. 3

The bars were submitted to an austempering heat treatment, which involved heating at 910°C for 1 h, followed by submerging the samples in a molten salt bath, where the samples were held at 360°C for 90 min. Tensile test samples of 6·35 mm in diameter (ASTM A536-84) were machined from the heat treated bars. (Fig. 1*a*).

Tensile testing was carried out using an Instron series IX automated material testing system. The experimental set-up used to test coated and uncoated tensile samples is shown in Fig. 2. A section of a plastic pipe surrounds the calibrated section of the tensile sample. A rubber stopper is clamped at the bottom of the pipe, and this is filled with tap water before starting the test. Reported values are the average of at least three tests.

Different alternatives of available protective coatings were analysed and applied to ADI samples.

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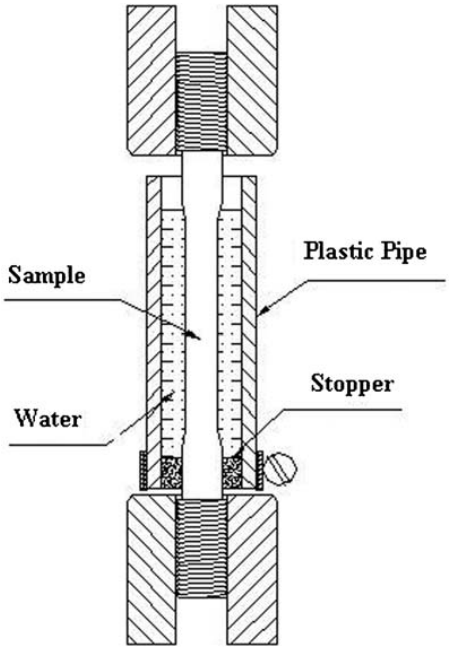


2 Experimental set-up

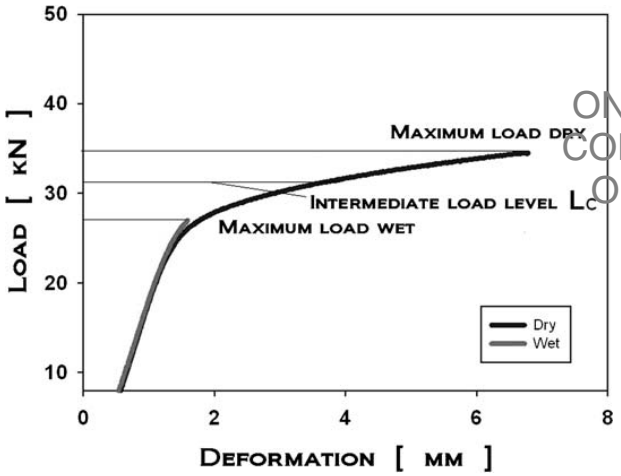
Taking into account several practical application possibilities on the sample surface, the following coatings were selected:

(i) electrolytic and mechanical galvanising
(ii) electrolytic and mechanical zinc
(iii) polyester
(iv) polyester urethane
(v) self-cured epoxy
(vi) heat cured polyester epoxy
(vii) acrylic fibre.

The zinc layer was applied by an electrolytic process through an alkaline bath with pH 13 during 20 min, obtaining a layer of $\sim$20 μm. The hybrid epoxy–polyester is a powder paint applied by means of an electrostatic charge at 200°C for 45 min. Before paint application, a phosphatising treatment was conducted at room temperature. Phosphatising produces a thin corrosive protection layer and provides an excellent substrate for paint application.

Polyester and polyester urethane paintings were applied in the same manner.

The self-cured epoxy and fibre acrylic paints were hand applied after a careful surface cleaning using carbon tetrachloride.



ONLINE COLOUR ONLY

3 Intermediate load L_C

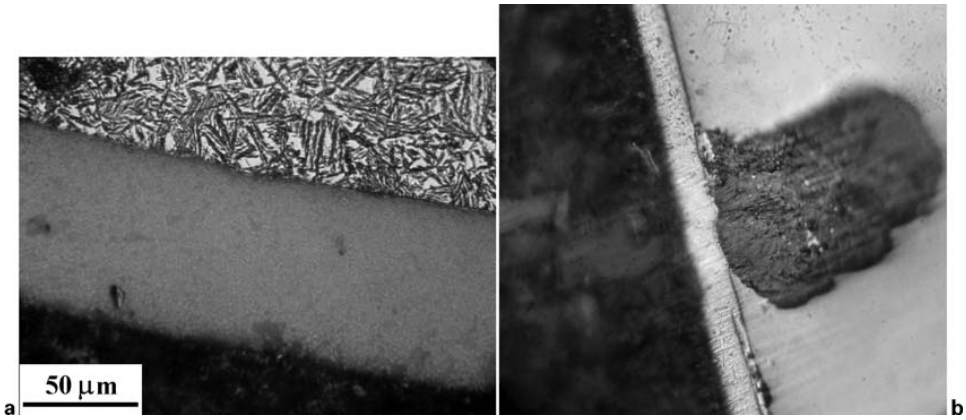
The thicknesses of different protective layers used to coat the surface of the tensile test samples was measured by light microscopy, and the values obtained are listed in Table 2.

With a view to evaluating preferential crack initiation sites at early stages of plastic deformation from the unalloyed melt, a group of samples were grinded longitudinally to obtain a plane face, which was polished to carry out metallographic observations (Fig. 1*b*). Before the tensile testing, some microscopic fields of the sample calibrated zone were documented with photographs. The next step was load application in dry conditions until an intermediate load L_C lower than the maximum load in dry conditions (C) but higher than the maximum load in wet condition (B) was applied in dry conditions (Fig. 3). Afterwards a second set of photographs of the same zone was obtained. The final stage of the test consisted in loading and holding the sample at the same intermediate load L_C and then touching the surface with a wet cotton swab causing the instantaneous breakage of the sample. A final set of pictures was obtained after such breakage. Fracture surfaces were examined by means of SEM.

Results and discussion

Use of protective layers

The microstructure of the DI used in this investigation showed graphite spheroids that reached sizes of 50 μm.



a H-epoxy; *b* E-tin

4 Micrographs of transverse cuts of coated tensile samples

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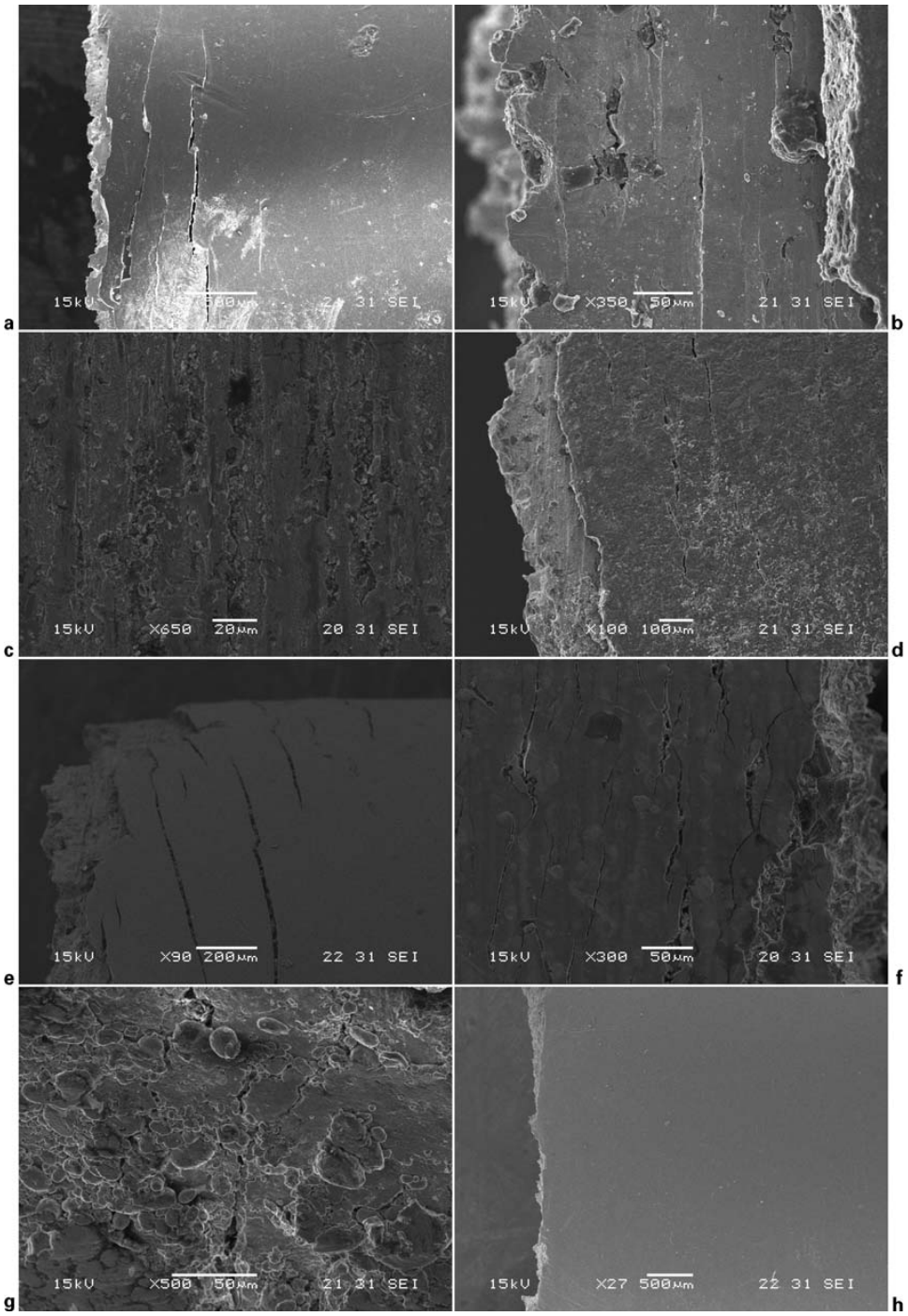

a S-epoxi polyester; *b* H-epoxi; *c* E-tin; *d* polyester; *e* polyester–uretane; *f* E-zinc; *g* M-zinc; *h* F-acrylic

5 Lateral surface of coated samples near fracture

As a result, the surface of the tensile test samples included a number of graphite particles. As the thickness of the applied coatings was similar to or smaller than the diameter of the graphite nodules, it seemed reasonable to verify the ability of the different paints and coatings to fully coat the surface of the samples, avoiding water contact with ADI surface. Figure 4 depicts the polished section of coated samples where the exposed surface of the graphite nodules appeared fully coated. This was the case for all the types of coatings used in the present study.

The coated portions of the surface of the tensile samples were also examined with SEM before tensile testing. A smooth even surface was observed in all cases, indicating that all tested surfaces were homogeneously coated before tensile testing.

Table 3 lists the results of tensile tests. Results of tests carried out on uncoated samples in contact with air and water are included for comparison purposes and assessment of the extent of protection. The results of testing in air largely satisfy grade 900-650-09 of ASTM A897M-06, whose minimum values are also listed in Table 3. As a result of water contact, uncoated samples showed a very noticeable decrease in both tensile strength and elongation, while yield stress remained fairly unchanged. The extent of embrittlement is similar to that reported earlier in several investigations.[1–7] Unexpectedly, Table 3 also shows that the use

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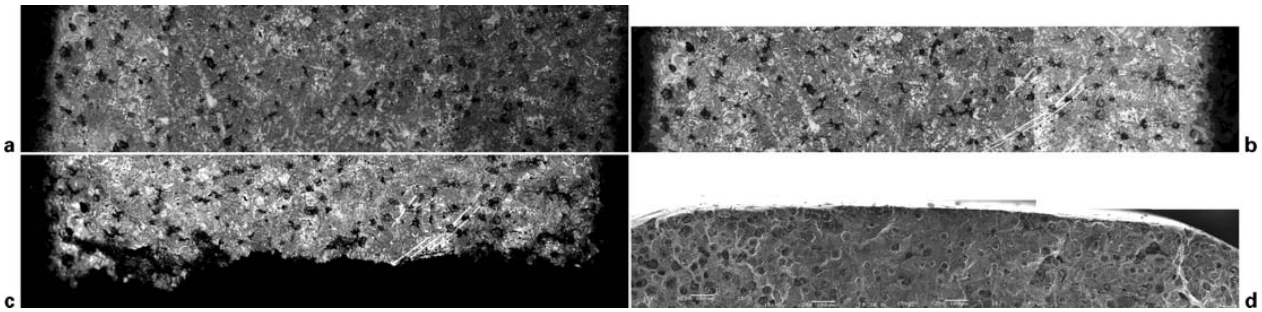
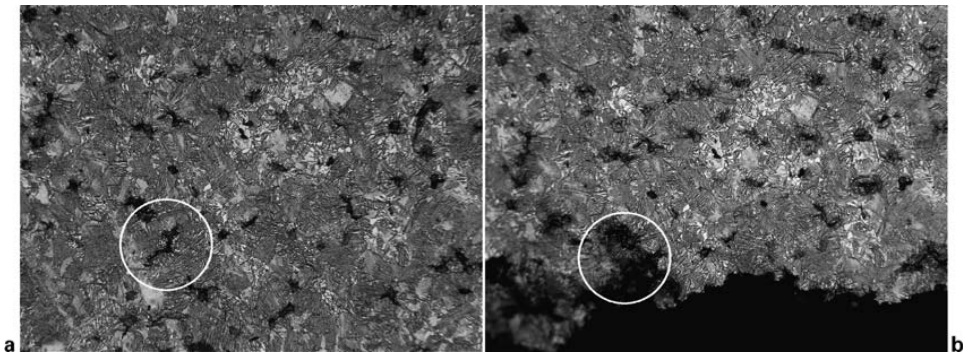


6 *a* lateral face of sample, *b* lateral face of sample alter loading at intermediate level L_C, *c* lateral face of sample alter induced break by mean of cotton swab and *d* fracture surface of sample



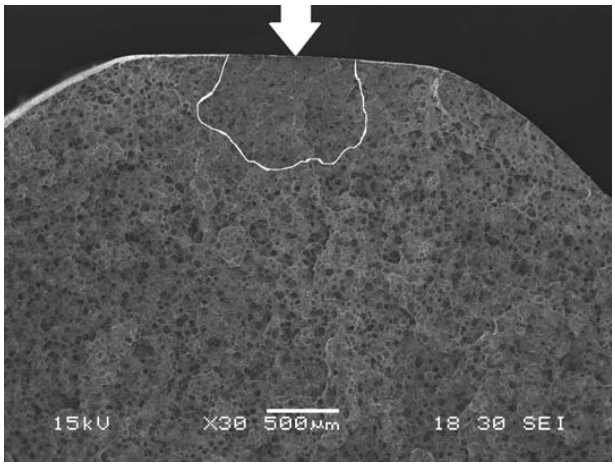
a after loading to L_C; *b* after induced fracture

7 Cracks developed at LTF zones

of paints and metallic coatings made little or no contribution to reduce the drops in tensile strength and elongation caused by water. In fact, some of the results indicate more intense embrittlement on the coated samples. Only mild increases in elongation were obtained after coatings were used. Polyester-U paints showed the largest, though still modest, protective effect, causing the elongation to increase from 1·2% in the uncoated sample to 4%.

Only acrylic coatings loaded with fibres worked against embrittlement. It is apparent that, for a coating to be effective, it must be able to withstand relatively large deformations.

The integrity of the coating layers after tensile testing was inspected by SEM. Figure 5 displays the representative behaviour of tensile sample surface at the fracture line. In all cases, transverse cracks were found on the coating near the fracture surface. This suggests that, as the sample is loaded, the applied coating breaks producing outside cracks. These cracks allow water to make contact with ADI metallic surface. The experimental set-up used does not allow verifying whether the coating breaks before the sample fractures or if both events take place simultaneously. Embrittlement occurrence at different degrees allows to suppose that the surface cracks are produced when the base metal is at the initial stages of plastic deformation and, hence, susceptible to embrittlement. Earlier investigations have shown that the sudden contact of water with the surface of samples stressed in air at levels above the ultimate tensile strength measured in contact with water causes an almost immediate fracture at the point of contact.[6] This seems to indicate that coating breakage is the controlling factor for sample fracture. Values listed on Table 3 suggest that both paints and metallic coatings tested break at strain levels between 1·3 and 4%.



8 Arrow points zone touched by cotton swab inducing instantaneous fracture

These results indicate that most of the paints and metal coatings used in the present study did not protect ADI from water embrittlement, as they developed cracks during straining. When this occurs, the sample fails instantaneously (as observed with the test conducted in the following section) at constant load, when putting the sample in contact with water.

The protection method is effective when the layer integrity is not affected by the deformation undergone by the substrate. In other words, when crack formation is avoided and water penetration is inhibited, there is no contact with the ADI surface. 4

Another attempt to protect ADI against embrittlement, based on the preliminary test conducted, was to spray the tensile samples with the antirust and lubricant WD40. This product's name is an acronym for 'water

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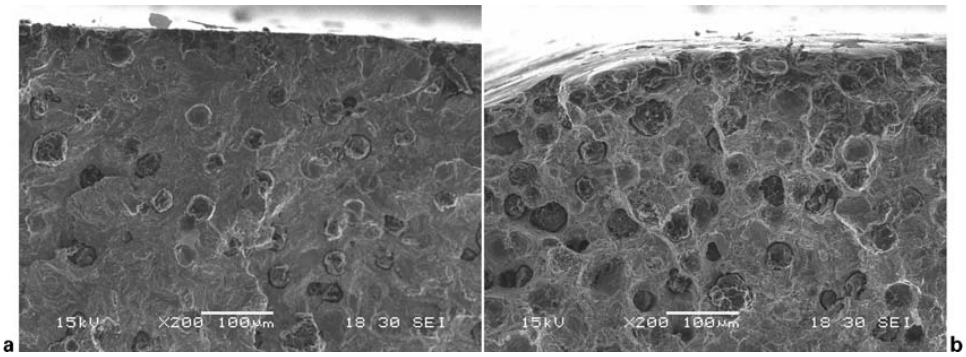

a brittle fracture; *b* ductile fracture

9 Characteristics of fracture surfaces

displacement – attempt number 40'. This led the authors to use it to displace water from the crack generated at the first stages of plastic deformation.

After spraying the samples, they were submerged and tested, and no signs of embrittlement were observed.

Evaluation on unalloyed samples

The results of the tensile tests are displayed in Table 4. Dry test results show that melt SA presents values slightly lower than those required by the standard ASTM 897-06 for ADI grade 1.

The SA cast values for strength and elongation in wet conditions indicate a significant reduction with respect to those of dry values. Drops reached values of 15 and 80% respectively, while yield stress remained at the same level.

As opposed to what was hypothesised, the use of non-alloyed DI with minimised LTF zones neither inhibited nor reduced the embrittlement phenomenon.

It could be concluded that the addition of alloy elements is not detrimental from an embrittlement perspective.

The supposedly cleaner LTF zones present in an alloy free cast is still able to generate cracks at the early stages of plastic deformation, which acts as the nucleation centre from the start of the water embrittlement process.

A better explanation is provided by the microstructural analysis of the samples with a grinded surface, which is displayed in Fig. 6 at different stages. Figure 6*a* illustrates the sample before applying any load; the ausferritic matrix as well as the LTF zones and graphite nodules can be observed. The same fields are shown in Fig. 6*b* after loading the sample with an intermediate load L_C between the dry and maximum loads and stopping the test (as observed in Fig. 3). Finally, Fig. 6*c* shows the same zone after the fracture caused by loading the sample, again at the same level L_C and touching it with a cotton swab, inducing the instantaneous breakage, which obviously initiates at the contact point. Finally and completing the sequence, Fig. 6*d* provides a macrography of the fracture surface.

The study of the lateral surface after loading the samples with load L_C at higher magnification reported nucleation and growth of cracks in LTF zones (circle in Fig. 7*a*). The line of fracture is observed in Fig. 7*b* where the crack mentioned plays a key role after being touched by the wet cotton swab.

These observations demonstrate that the initiation of cracks on unalloyed DI proceeds in the same manner as that previously verified in low alloy DI, thereby indicating that suppressing the alloy elements in the melt does not improve the strength of LTF zones nor prevents crack initiation.

Figure 8 displays the fracture surface of the same sample at different magnifications, and the arrow points at the location at which the sample surface has been touched with the cotton swab. A nearly round, bright and flat fracture area, of $\sim$1 mm diameter, appears to originate in such location. The examination of the fracture surface in this zone shows that the fracture mechanism characteristic of the flat regions is cleavage, as shown in Fig. 9*a*. The fracture surface shows graphite nodules and spherical holes left by nodules that remained on the opposite surface.

Brittle fractures are generally associated with smaller and more localised strains than those associated to ductile fractures.

Aqueous environments are supposed to weaken interatomic bonds at the crack tip producing a more localised microvoid coalescence process. In such fracture mechanism, the nucleation of dislocations is facilitated. In this manner, dislocations are injected from the crack tip on suitable inclined slip planes, which produces a faster crack advance.

Once the fracture process starts in the manner described, the sample fails due to overload, generating a different fracture surface produced by a different mechanism. The fracture surface beyond the flat portion is shown in Fig. 9*b*, which displays a predominantly ductile fracture, characterised by dimples. Nevertheless, some small areas of cleavage are also present, producing a fracture type commonly referred to as quasi-cleavage,[12,13] as those typically found in samples tested in air. The marked difference in the brittleness of both fracture types is also emphasised by the extent of plastic deformation around the graphite nodules, which is much greater on the quasi-cleavage fracture.

Conclusions

1. From a good number of protective coatings applied on the tensile samples tested, only one was able to protect the sample under stress from water contact, thus preventing the embrittlement phenomena. The protection method is effective when the layer integrity is not affected by the deformation undergone by the substrate. In other words, when crack formation is avoided and water penetration is inhibited, there is no contact with the ADI surface.

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2. The well known antirust and lubricant WD40 proved to effectively protect against water contact. That is to say, WD40 is suitable for water displacement into cracks generated in early stages of plastic deformation, thus preventing the classic fracture process of the water embrittlement process.

3. The amount of alloy elements present in the melt does not influence the embrittlement degree of the samples, i.e. a stronger microsegregation in the LTFs does not affect the amount of embrittlement.

4. Unalloyed DI tested under tension developed superficial cracks in the same manner that alloyed DI did. The fracture mechanism is based on the fact that aqueous environments weaken interatomic bonds at the crack tip producing a more localised microvoid coalescence process. In such fracture mechanism the nucleation of dislocations is facilitated, inducing a faster crack advance.

Acknowledgement

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