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Environmentally assisted embrittlement of ADI by contact with liquids

*R.A. Martínez, S.N. Simison and R.E. Boeri

INTEMA - National University of Mar del Plata – CONICET, Mar del Plata – ARGENTINA

Austempered ductile iron (ADI) suffers an uncommon embrittlement process when it is stressed above its yield strength in contact with water and other liquids. The advances in the understanding and characteristics of this environmentally assisted embrittlement process, since it was first reported, are summarised. The extent of embrittlement for different ADI strength grades is characterised. The influence of various liquid environments is discussed. The features of the fracture surfaces are also analysed. Recent results of testing under applied potential are presented. An explanation of the fracture mechanism is proposed, based on the recent identification of cracks which developed in the last to freeze portions as a result of plastic deformation.

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Keywords: ADI, embrittlement, water, liquids, fracture.

Introduction

Austempered ductile iron (ADI) is applied widely for the fabrication of cast parts for rail-road, automotive, agricultural and other industries. Since ADI combines excellent strength and good ductility with low cost and the ability to produce nearly finished parts through casting, it is increasingly used to replace parts traditionally made of cast, forged or machined steels of different grades. ADI can be produced in different grades, reaching minimum properties ranging from 850 MPa to 1600 MPa of tensile strength, and elongation between 10 and 0% respectively¹. A large number of successful applications of ADI have been made since the early 70's, and ADI gained a reputation as a reliable material. Nevertheless, during the late 90's, Shibutani et al.² and Komatsu et al.³ reported that ADI mechanical properties are severely affected when the material is stressed with its surface in contact with water, leading to drastic drops in tensile strength and elongation. Environmentally induced cracking or embrittlement of this nature are not frequent, nor are they thoroughly studied, to the best of our knowledge.

Environmentally induced cracking

The most extensively studied processes of environmentally induced cracking (EIC) are hydrogen embrittlement (HE), stress corrosion cracking (SCC) and liquid metal embrittlement (LME).⁴ SCC is characterised by brittle failures in which cracks propagate at stress intensity (K) levels lower than the critical values in air or

vacuum, as a result of the combined effect of a tensile stress field and the presence of a corrosive media. Corrosion rates are usually quite low. The mechanisms involved in this type of failure are very complex and remain under discussion. In consequence the occurrence of SCC failures in service is still difficult to predict.

HE involves brittle fracture caused by penetration and diffusion of atomic H into the crystal structure of an alloy. The kinetics of hydrogen generation are accelerated by an increase in the cathodic polarisation. Thus, cathodic polarisation should enhance HE, while anodic polarisation should have the opposite effect.

LME causes the catastrophic brittle failure of normally ductile metal alloys when coated by liquid metal and stressed in tension. The fracture mode changes from a ductile to a brittle intergranular or brittle transgranular (cleavage) mode. It has been shown that the stress needed to propagate a sharp crack or a flaw is significantly lower than that necessary to initiate a crack in the liquid metal environment. In most cases, the propagation of cracks appears to occur instantaneously, with the fracture propagating through the entire test specimen. The velocity of crack or fracture propagation has been estimated to be 10 to 100 cm/s. LME is not a corrosion, dissolution or diffusion-controlled intergranular penetration process. The embrittlement is severe, and the propagation of fracture in the case of LME is very fast as compared to that in stress corrosion cracking.⁴

Characteristics of the embrittlement of ADI

The reports of Shibutani et al.² and Komatsu et al.³ show that ADI suffers environmentally assisted embrittlement (EAE) when it is strained above its yield strength while in contact with water. This effect was verified both for tensile testing and bend testing of pre-cracked samples. Later, Martínez et al.⁵ obtained similar results in an independent laboratory, while testing ADI samples of different chemical composition and strength grades. These investigations showed that ADI suffers significant reductions in UTS and elongation that can reach up to 30% and 70% respectively, when tested in tension, as shown in Fig. 1. This drop of mechanical properties takes place almost instantaneously, and it reverses immediately when the surface of the sample is dried.² On the other hand, impact properties are not affected by contact with water, which suggests that the EAE does not act under high loading rate^{2,3}. The EAE not only affects ADI, but also ductile irons (DI) of other microstructures, such as those having martensitic and pearlitic matrices. All investigations showed that the higher the strength of the DI, the larger the drop in

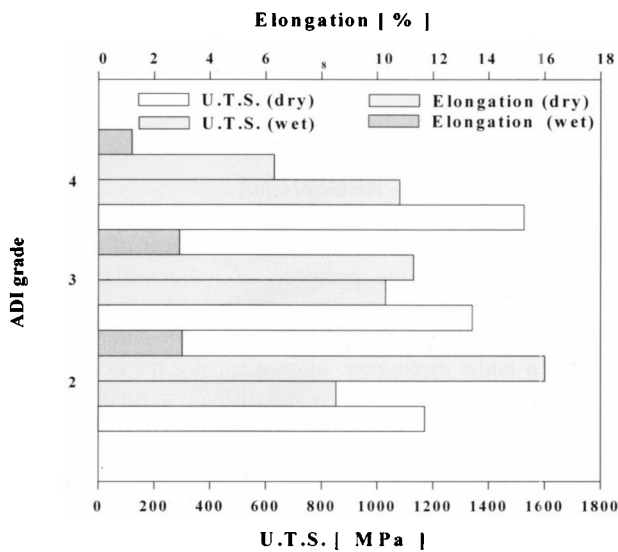


Fig. 1 Change in UTS and elongation as a result of tensile testing of ADI grades 2, 3 and 4 in contact with water.⁵

strength and elongation. Only ferritic matrix ductile iron has been found to be immune to this type of embrittlement.^{2,3}

The characteristics of the embrittling effect caused by water on contact with ADI are quite unique, not corresponding with any other EIC reported for metals.

Shibutani et al.² and Komatsu et al.^{3,8} proposed that the drop of ADI properties is caused by hydrogen embrittlement. They suggest that the effect is induced by the generation of hydrogen atoms from water on the ductile iron surface under plastic deformation. Hydrogen atoms would then diffuse into the ductile iron matrix, causing the embrittlement. This affirmation was supported by the results of tensile testing in a H₂ atmosphere, which caused similar embrittlement to that caused by water. Nevertheless, the mechanism by which the protons would reduce at the water/ADI interface causing an almost instantaneous effect has not been explained, nor has the presence of hydrogen been verified.

Martínez et al.⁵ found that ADI is also embrittled by other liquid environments, such as isopropyl alcohol and SAE 30 mineral lubricant oil, as shown in Fig. 2. The severity of the embrittlement caused by alcohol and oil is less significant than that of water. On the other hand, contact with the very strong wetting agent WD40TM did not cause embrittlement. The embrittlement effect of SAE 30 lubricant oil is certainly unexpected, since mineral oils are generally used to protect the surface, and are regarded as inert media for environmentally assisted cracking tests. Martínez et al.⁵ examined the role of hydrogen on the embrittlement. To do this, they first carried out tensile tests with the ADI surface in contact with water based solutions of pH ranging from 5.5 to 11.9. The results showed that the degree of embrittlement was constant, regardless the pH of the solution. Later, Masud et al.⁷ also examined the role of

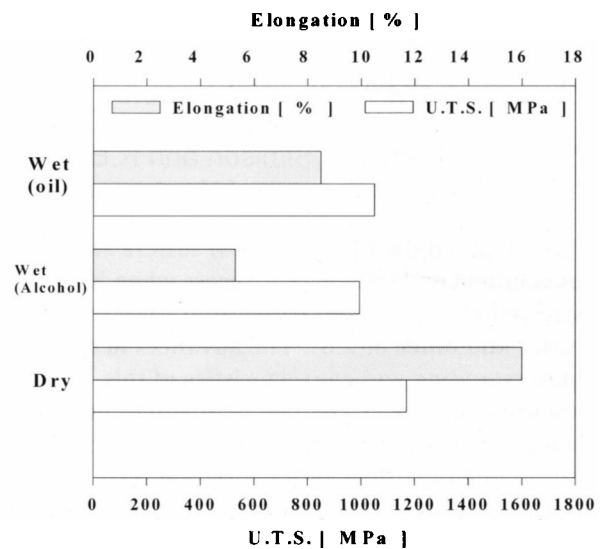


Fig. 2 Change of UTS and elongation caused by contact with lubricant oil and isopropyl alcohol.⁵

hydrogen in ADI embrittlement by using a more effective methodology. They investigated the behaviour of ADI on tensile testing in aqueous media under controlled electrochemical conditions, aiming to identify whether the loss of ductility can be either inhibited or enhanced by stimulating or avoiding the reduction of protons at the sample's surface. They used ADI grade 2 (ASTM A 897M-90) tensile test samples. The values of controlled potential applied during tensile testing were chosen based on the results of polarisation curves. A potential of -1.45 V (SCE) was used to induce cathodic conditions, in which the generation of hydrogen on the surface is stimulated, and a potential of -0.55 V (SCE) was used to inhibit hydrogen generation. Their results showed that the magnitude of the embrittlement effect caused by water is not affected by the application of a controlled potential. These results clearly contradict earlier results of other authors^{2,3}, and suggest that the EIC of ADI is not an electrochemical phenomenon, since neither cathodic nor anodic applied potentials have been able to inhibit or to enhance embrittlement.

Role of microstructure

Martínez et al.⁵ analysed the role of the different microconstituents of the matrix on the EAE effect. They showed that there is no definite base to link the presence of a given microconstituent in the microstructure with the susceptibility to embrittlement. Other factors, not just the phases forming the matrix, could affect EAE, such as the presence of interfaces and chemical or microstructural inhomogeneity.

An analysis of the effect of the matrix inhomogeneity on EAE has been recently made by Laine,⁶ who aimed to identify the fracture initiation site of ADI embrittled by contact with water. He examined the surface of the tensile samples during the fracture process. Square section tensile samples were used. Sample faces were

polished metallographically before testing. It has been shown that microsegregated regions of the ADI microstructure, usually referred to as Last To Freeze (LTF), cracked during testing after plastic deformation starts, as shown in Fig. 3. Cracks of width ranging from 30 to 170 μm were observed on the sample surface.

The microstructure of LTF regions after austempering may show, depending on the chemical composition of the DI and the heat treatment practice, different amounts of unreacted austenite, martensite and even small carbides precipitated during solidification or heat treatment. With this microstructure, LTF regions are usually harder and more brittle than the matrix. This may account for the cracking LTF when the plastic deformation of the surrounding austempered matrix imposes relatively large stresses on them, as shown by Laine.⁶ It is known that the degree of inhomogeneity in the LTF and its extent are affected by the chemical composition of the iron, by the solidification rate, and possibly by the nodule count. Additionally, austempering heat treatment variables also influence the homogeneity of the microstructure at the LTF. Therefore, the quality of ADI may affect the intensity of the EAE caused by water. The validity of this speculation has not been verified yet.

Fracture mechanism

The fracture surface of the embrittled samples has been examined by Komatsu et al.³ and Martínez et al.⁵ Small and randomly distributed regions of cleavage fracture are present in most fracture surfaces of ADI tested in air, conforming to a fracture mechanism called quasi-cleavage. The fracture surfaces of tensile test samples tested in contact with embrittling liquids show a larger proportion of cleavage facets than the fracture surface of samples tested in air. Both Komatsu and Martínez identified flat bright portions covering a fraction of the fracture surface of the tensile samples tested in water. These bright portions corresponded primarily to areas of cleavage fracture.

Masud et al.⁷ investigated the connection between the flat fracture regions on the fracture surface of tensile

testing samples, and the fracture initiation site. In an attempt to localise the initiation of the fracture, the tensile sample surface was put in contact with water only at a very small location, by using a dropper previously wet with water. This was done after stressing the sample up to a stress level greater than its tensile strength in contact with an aqueous solution, but lower than the dry tensile strength. Under this stress condition, contact of the wet dropper with the sample surface caused the fracture to take place instantaneously. Fig. 4 shows a macrography of the fracture surface. The arrow points the location at which the sample surface has been touched by the wet dropper. A nearly round, bright and flat fracture area, of approximately 1mm diameter, originates from the point of contact of the dropper. The examination of the fracture surface by scanning electron microscopy showed that the fracture mechanism characteristic of the flat region is cleavage, as shown in Fig. 5. The fracture surface out from the flat portion, Fig. 6, shows a predominantly ductile fracture, characterised by dimples. 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 for the predominantly ductile fracture. The results proved that water induces brittle cleavage fracture of ADI. The results also show that the location of flat and bright fracture portions that are observed on the fracture surface of tensile samples tested in contact with water, indicate the location of the fracture initiation.

Laine⁶ also analysed recently the fracture initiation and propagation, using similar methodology to that of Masud et al.⁷, but working on square section tensile samples of polished surfaces. The surface metallography of the whole sample was photographed before testing. After the sample was broken in contact with water, the surface fracture path could be observed. Laine found that fracture initiates at the LTF regions of the sample, which became cracked during the test at stress levels surpassing the yield strength of this ADI. The observation of the fracture surface by Scanning Electron Microscopy showed those LTF regions fractured by cleavage.

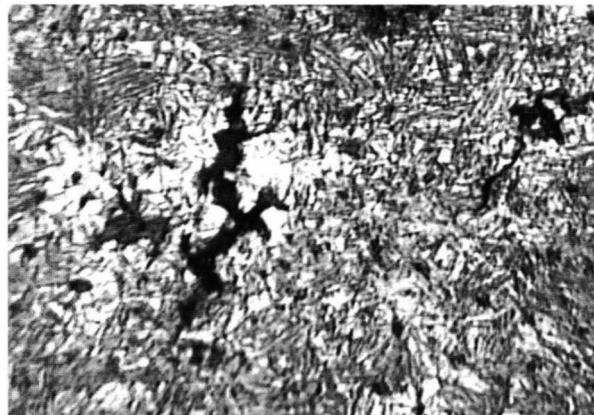


Fig. 3: Typical cracking of LTF regions of ADI samples after plastic deformation.(1000X)

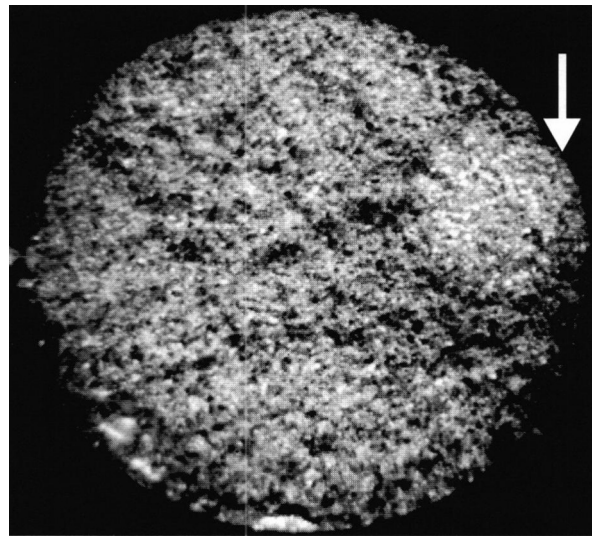


Fig. 4 Fracture surface of a tensile test specimen. The arrow points the location at which the sample was wet. Sample diameter is 6.5mm.

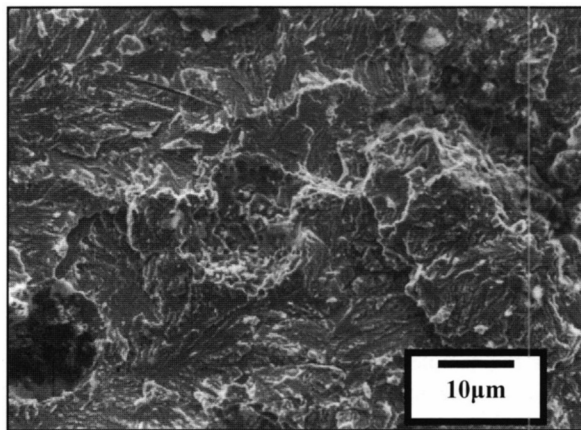


Fig. 5 Fracture surface of ADI embrittled by water.

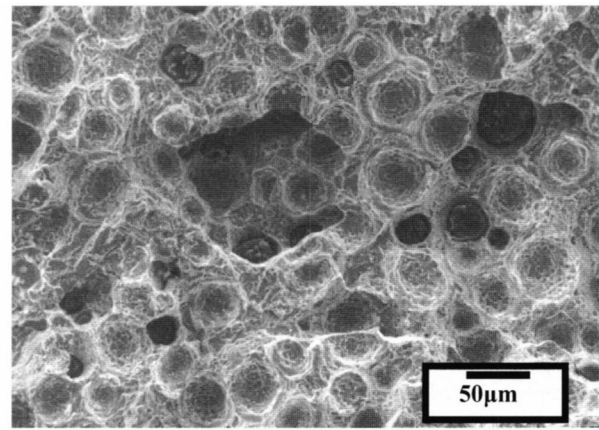


Fig. 6 Predominantly ductile fracture surface of ADI broken in contact with water, shown at a location far from the fracture initiation site.

Cause of embrittlement

The cause of embrittlement remains unknown. The initial suggestion of Shibutani et al.² and Komatsu et al.³, proposing that hydrogen was responsible for the embrittlement, has not been verified yet. Furthermore, the little dependency of the phenomenon with the time of exposure to water, and its fast reversibility, do not precisely agree with the usual characteristics of the hydrogen embrittlement effect. Additionally, the results of Martínez et al.⁵ and Masud et al.⁷ do not support the role of hydrogen as proposed by Shibutani and Komatsu, since neither the concentration of protons in the embrittlement media, nor the application of controlled potentials, affect the degree of embrittlement. Furthermore, the fact that other liquids, such as mineral oil and alcohol, cause embrittlement, suggest that the explanation of the effect should be based on the influence of other factors.

Proposed fracture mechanism

The current knowledge about EAE of ADI upon contact with water shows some similarities with LME: the propagation of cracks takes place almost instantaneously at a very fast rate, and the process appears to be independent from corrosion and dissolution events.

The authors propose that the fracture of ductile iron in contact with water proceeds as follows: upon stressing ADI at a certain level above its yield strength, it develops cracks at the LTF regions, as shown by Laine.⁶ When this takes place in contact with water or other liquids, the liquid penetrates the crack, the A-A atomic bonds at the crack tip are weakened by the chemisorption of an atom or molecule B, as shown schematically in Fig. 7.

The chemisorption process presumably takes place spontaneously or after the A-A bonds have been strained to some critical value. In any event, electronic rearrangement takes place because of adsorption, and weakens the bonds at the crack tip. When the applied

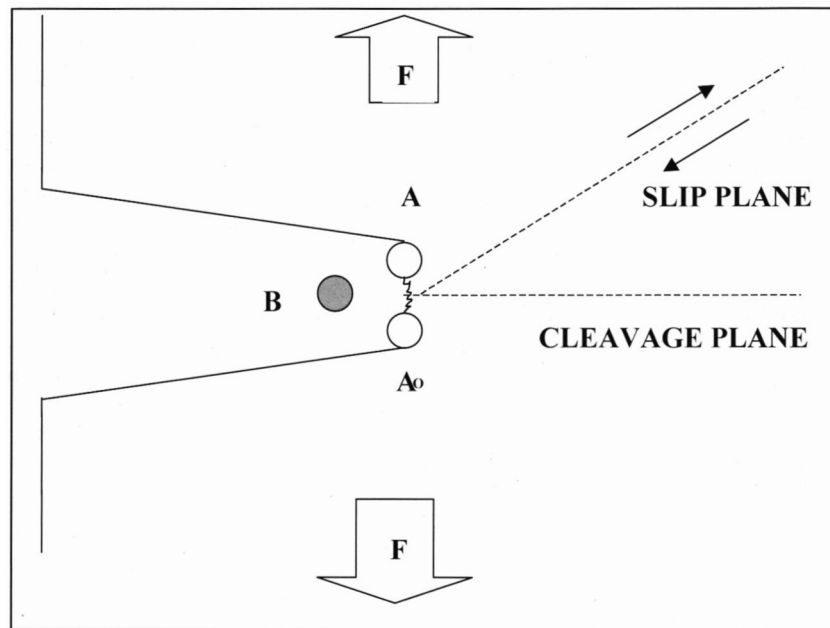


Fig. 7 Schematic representation of the weakening of A-A atom bonds at a surface crack tip as a result of the interaction with an atom or molecule B supplied by the surrounding liquid.

remote stress is increased so that local stress at the crack tip exceeds the reduced breaking strength of A-A bonds, then the crack becomes unstable and grows rapidly. Initially, the crack grows in a brittle manner, by cleavage, but changes to a ductile mechanism as it grows further from the fracture initiation site. Taking into account the load conditions in tensile testing, the stress levels and the sample dimensions, and assuming a semi-elliptical surface defect and a K_{IC} value of $90 \text{ MPam}^{1/2}$, the size of the critical defect can be estimated to be 0.8 mm. This would indicate that if the presence of water activates the rapid growth of a crack, and such a crack extends beyond the critical defect size, then, even when the fracture mode changes to a higher energy consuming mechanism, the remaining ligament will not be able to stop fracture and the sample will collapse. The size of the cleavage fracture surface observed in the tensile specimens fractured in contact with water used in this work, shown in Fig. 4, is usually of approximately 1.5mm. This size is greater than the critical defect size, supporting the proposed mechanism.

Preventive methods

Shibutani et al.² and Komatsu et al.³ proved that the embrittlement can be effectively prevented by painting the surface of ADI parts. They also proposed to avoid embrittlement by developing a layer of ferrite at the casting surface. Nevertheless, the use of such method does not seem to be advisable, since the presence of a surface layer of soft ferrite will favour the nucleation of fatigue cracks.

The effectiveness of other surface coating methods to prevent fluid embrittlement, different from painting, should be investigated.

Summary and concluding remarks

Water and other liquids cause the embrittlement of ADI. The characteristics of this environmentally assisted cracking effect are quite unique, and share some of the features of liquid metal embrittlement. The effect of the environment is not understood. Recent experiments do not support hydrogen embrittlement as the cause of fracture. An explanation of the fracture mechanism has been proposed by the authors, based on the recent observation of cracking of the last to freeze portions of the ADI microstructure upon straining.

The unusual embrittlement caused by lubricant oil deserves special attention. Many high strength ADI parts, such as crankshafts, gears and connecting rods, work in direct contact with mineral lubricant oils. A detailed characterization of the effect of different lubricant agents seems necessary, in order to identify those causing minimum detrimental effects.

Future work should be aimed at clarifying the mechanism of EIC responsible for the embrittlement of ADI. In particular, it is necessary to identify the role of the different liquids on fracture. Additionally, the influence of the ADI microstructure on EIC should be investigated.

Acknowledgement

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