Embrittlement of austempered ductile iron caused by contact with water and other liquids

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Recent research has reported that austempered ductile irons (ADI) suffer a marked embrittlement when the material is tested in tension with its surface in contact with water. The objective of this investigation is to verify that embrittlement phenomenon, and to characterise the behaviour of several strength grades of ADI. The embrittlement effect of other wetting agents is also investigated. The results verified prior studies. A noticeable decrease in UTS and elongation takes place when ADI samples of grades 2 to 4 are tested immersed in water. The embrittlement effect is not affected by the concentration of protons in water. Embrittlement of ADI was also found when testing in contact with isopropyl alcohol and SAE 30 lubricant oil. A very strong wetting agent (WD40™ oil) does not cause embrittlement. Pearlitic matrix ductile irons also suffer embrittlement in contact with water, while ferritic matrix ductile irons of the same chemical composition, do not suffer embrittlement. The present study advances in the characterisation of the embrittlement of ADI, and identifies new embrittling liquids, but does not provide a definite explanation for its causes.

Keywords: austempered ductile iron, embrittlement, water, fluids

Introduction

The austempered ductile iron (ADI) is an emerging engineering material that has excellent mechanical properties. It combines very high strength with good ductility and toughness, and very good wear resistance[1,2,3]. ADI has a rapidly rising number of successful applications in several fields, such as the heavy truck, railroad, agricultural and automotive industries.

However, recent work by Shibutani *et al.*[4] and Komatsu *et al.*[5] reported that ADI suffers a marked embrittlement when the material is tested in tension, with its surface in contact with water. Significant reductions in UTS and elongation were measured. The effect reverses soon after tensile samples are dried. The embrittlement effect caused by water in tension testing is not found in impact testing, indicating that there is a strain rate dependency.

The characteristics of embrittlement of ADI reported by Komatsu *et al.*[5] are not frequently found in metallic materials, to the best of our knowledge. Shibutani *et al.*[4] find similarities between the embrittlement of ADI and the behaviour of hydrogen embrittled materials, and conclude that this effect is induced by the generation of hydrogen atoms from water on the ductile iron surface after plastic deformation. Hydrogen atoms then diffuse into the ductile iron matrix, causing the embrittlement. This observation was further supported by the results of tension testing in an H_2 atmosphere, which caused an embrittlement similar to that caused by water. Nevertheless, the mechanism by which protons are reduced at the water/ADI interface, and cause an almost instantaneous effect, is not clear. Furthermore, the dependency of the phenomenon on the time of exposure to water, and its fast reversibility, do not precisely fit the usual characteristics of the hydrogen embrittlement effect.

This embrittlement phenomenon is not simply of academic interest, but also has great importance for the safe industrial application of ADI. Although failures of ADI involving brittle fracture in service have not been reported, there is a clear need to identify the mechanism and its influence on the behaviour of ADI in service.

The objective of this investigation was to verify the embrittlement phenomenon identified by Shibutani *et al.*[4] and Komatsu *et al.*[5], in an independent laboratory and on a different base ductile iron. The embrittlement of several strength grades of ADI were also investigated. Additionally, the embrittlement effect of other wetting agents, such as water based solutions with different pH and other fluids, like oil and alcohol, were also tested. The fracture surface is examined by SEM to identify the governing fracture mechanisms.

Experimental methods

Samples used in this study were obtained from one inch "Y" blocks[4] of an industrial ductile iron heat produced in a medium frequency induction furnace. The chemical composition is listed in Table 1. The iron showed a 100% nodularity, and 120 nod/mm^2 of size 5.[6]

For evaluation of tensile properties specimens of $\frac{1}{4}$ inch diameter (6.35 mm)[7], were used.

Ductile iron samples were heat treated to obtain ADI grades 2, 3 and 4[8]. ADI grade 2 was obtained by austenitizing at 900 °C for 60 minutes, followed by austempering in a molten salt bath held at 360 °C, for 90 minutes. ADI grades 3 and 4 were obtained by austenitizing at 910 °C for 60 minutes, followed by austempering temperatures of 320 and 280 °C, for 90 and 120 minutes respectively.

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Table 1 Chemical composition (%) of spheroidal graphite cast iron

C	Si	P	S	Mn	Ni	Cr	Mo	Cu	Mg
3.20	3.30	0.03	0.01	0.2	0.68	0.06	0.09	1.00	0.03

Other samples of the same heat were heat treated to obtain fully ferritic (680 °C for 24 hours followed by furnace cooling) and fully pearlitic matrices (austenitizing at 910 °C for one hour followed by air cooling).

Tensile specimens in the wet conditions were tested using an assembly composed by a section of a plastic pipe located surrounding the sample, and a stopper located at the bottom of the pipe (Figure 1). The pipe can be filled with the selected wetting agent, leaving most of the surface of the calibrated section of the test sample submerged in the fluid. The configuration of the assembly made it impossible to use existing extensometric devices. As a result, only UTS and elongation values are reported. The values of mechanical properties reported are average of at least three tests.

Tests were carried out for the following wetting agents: tap water, distilled water, water solutions with pH of 5.5 [H_2SO_4-water], 8.5 and 11.9 [Na(OH)-water], lubricant oil, WD40$^{(TM)}$ and isopropyl alcohol (99%).

Fracture surfaces were examined using a scanning electron microscope.

Results and discussion

Figures 2 and 3 show the ultimate tensile strength and elongation of three grades of ADI under study, tested in the dry condition and in contact with tap water. The UTS of all ADI grades tested suffered a marked decrease due to contact with water, lowering the strength to between 70 and 75% of the value in the dry condition. The elongation dropped more markedly, reaching values as low as 25 to 15% of the reading in dry testing. The results were identical when distilled water was used instead of tap water. The magnitude of the embrittlement effect observed is similar to that reported by Komatsu *et al.*[5] for ADI grade 1.

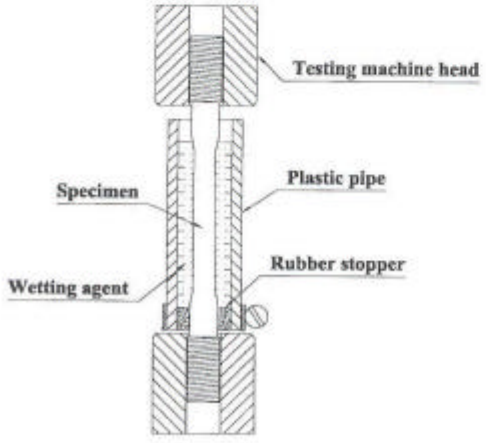

Fig. 1 Assembly used to carry out the tests

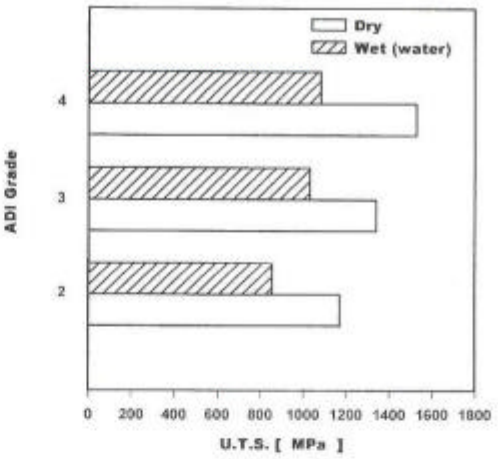

Fig. 2 Ultimate Tensile Strength of different ADI grades in dry and wet conditions

If the embrittlement phenomenon were caused by hydrogen, as suggested by Komatsu *et al.*[5], the concentration of protons in the aqueous media could affect the mechanical behaviour. To examine this hypothesis, ADI grade 2 tension samples were tested using water solutions having pH values ranging from 5.9 to 11.9 as wetting agents. The results are shown in Figure 4. Clearly, the change in the concentration of protons in the water solution does not cause a noticeable change of the embrittlement effect within the range of pH investigated. This finding does not seem to support a hydrogen embrittlement effect.

The use of isopropyl alcohol (99%) as wetting agent also causes embrittlement on ADI grade 2, as shown in Figure 5. The embrittlement is less pronounced than that caused by water. Reductions in strength and elongation of about 15% and 77% respectively were measured. Embrittlement effects caused by contact with methanol and other types of alcohol at room temperature are known for other metallic materials.[9,10]

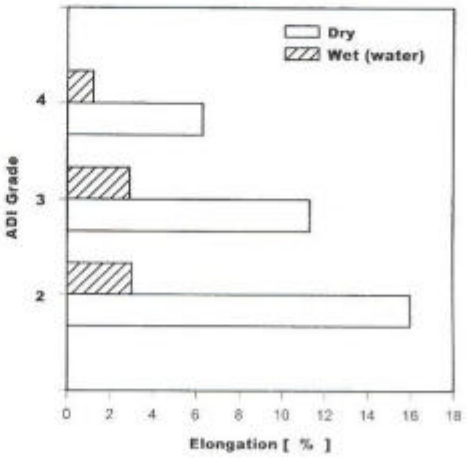

Fig. 3 Elongation of different ADI grades in dry and wet conditions

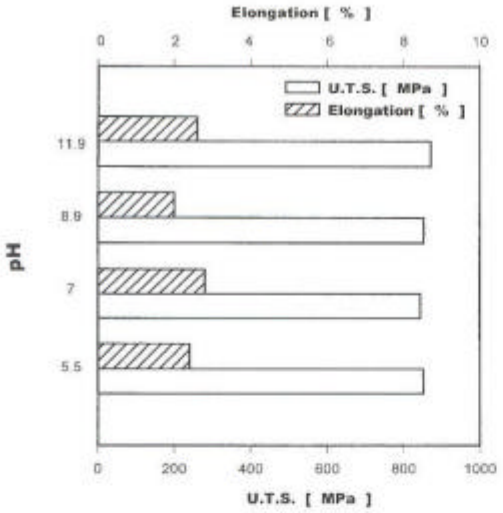

Fig. 4 U.T.S and elongation using different pH solutions (ADI grade 2)

Since all the wetting agents tested to this point of the study caused some degree of embrittlement, and considering that many machine components work in contact with some lubricant agent, it seemed advisable to test the influence of lubricant oil on the mechanical behaviour of ADI. This was done by filling the cell with SAE 30 lubricant oil. The test samples were in contact with the atmosphere and appeared to be dry before they were immersed in oil. The results of tensile testing of ADI grades 2, 3 and 4 are shown in Figures 6 and 7. Very surprisingly, the UTS suffered a small, but consistent decrease of between 2 and 10%, and the elongation showed a more marked decrease of between 29 and 42%. The embrittlement effect of oil was lower for the higher strength grade of ADI. These results are certainly surprising, since lubricant oils are generally used to protect the surface, and are considered to be inert media for

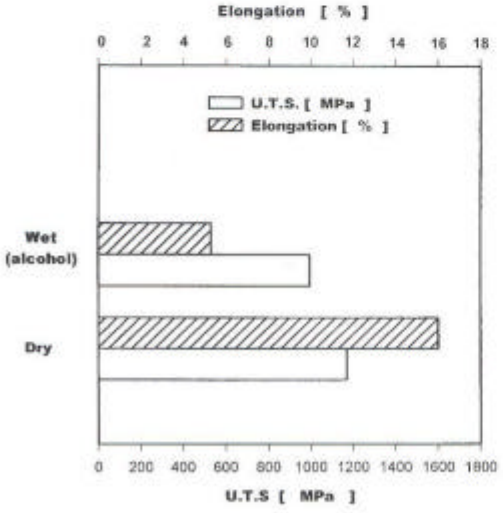

Fig. 5 U.T.S and elongation using alcohol as wetting agent (ADI grade 2)

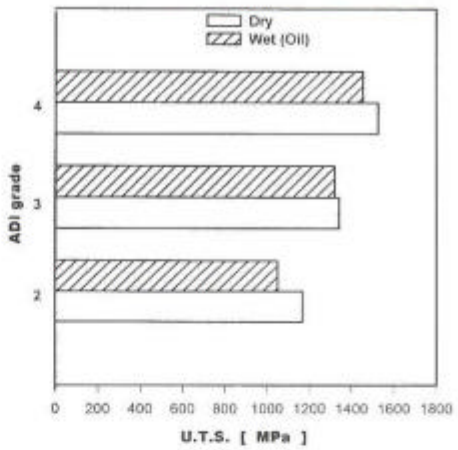

Fig. 6 Influence of SAE 30 lubricant oil on U.T.S

environmental assisted cracking tests. This suggests that the presence of minute amounts of water absorbed on the ductile iron surface, not removed before coating with lubricants, may still cause embrittlement. If such is the case, one should assume that small amounts of water are always present on the surface of the sample. The question is, why would such water cause embrittlement when covered by lubricant oil, and show no effect when the sample is in contact with the atmosphere? Attempts were made to remove any water possibly absorbed at the surface of the apparently dry samples, by two methods. First, a strong wetting agent capable of displacing water from cavities, such as WD40^{TM}, was used. The results were similar to the results for dry samples, indicating that no embrittlement is caused under this condition. Secondly, the apparently dry sample was heated up to 150 °C during 20 minutes, then coated with lubricant oil before it cooled down to room temperature to avoid any re-absorption of water, and tested in tension wetted by lubricant oil. The results were similar to those recorded for SAE 30 lubricant oil applied on the dry test sample. The results of these tests do not bring any conclusive evidence.

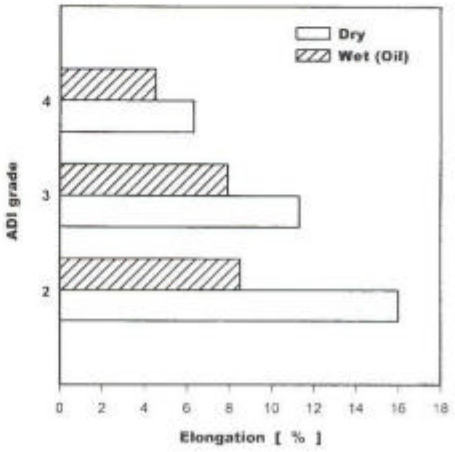

Fig. 7 Influence of SAE 30 lubricant oil on elongation

At this point of the investigation, the cause of the embrittlement effect of the different liquids tested remains unexplained. The hypothesis of hydrogen being responsible for the problem is not fully supported by some of the current experiments, since the concentration of protons in the media does not affect the mechanical behaviour, and the phenomenon also takes place in oil, where the action of mechanisms of environmentally assisted cracking is usually considered to be impossible.

The embrittlement of other matrix microstructures obtained on the same base ductile iron was also examined. The results of high strength pearlitic ductile iron, and of high ductility ferritic ductile iron are shown in Figure 8. The pearlitic DI suffers a noticeable embrittlement, while the ferritic iron retains its original strength and ductility. This agrees with the observations of Shibutani *et al.*[4]

An environmentally assisted cracking process could be the cause of the embrittlement. Such processes are usually very dependent on time. At a relatively high rate of loading, cracks may not have sufficient time to form, and the material will not be embrittled. This has been already observed by Komatsu *et al.*[5] On the other hand, a very slow loading rate could lead to increased embrittlement. This was examined by testing tensile samples using a very slow loading rate, of approximately 2 N/sec, in the plastic deformation region. The results are not different from the regular tension testing obtained at loading rates of about 30 N/sec.

The role of the microstructure on embrittlement is also not clear. Embrittlement has so far been identified on matrices composed of ferrite and austenite (ADI), ferrite and cementite (pearlite) and tempered martensite[4] (fine dispersion of carbides on a ferritic matrix). On the other hand, the phenomenon does not take place on a ferritic matrix. Furthermore, in high silicon steels having a bulk composition similar to that of the chemical composition of the ductile iron matrix (0.55–0.65C; 1.8–2.2Si; 0.7–1Mn), embrittlement is also present in the bainitic microstructure, but only causes a reduction in elongation[4]. It is clear that the microstructure affects the embrittlement, but it is difficult to identify the cause. The graphite cannot be clearly linked to the effect, since embrittlement is also detected in steels of similar composition that are free from graphite, and is not detected in ferritic ductile iron, in which plenty of graphite exists. Austenite can not be the cause of embrittlement, since it is only present in ADI matrix, and other microstructures not showing austenite are also affected. Cementite and carbides are present in embrittled pearlite and tempered martensite. Some investigators suggest that very small transition carbides are present in the microstructure of ADI. Carbides are certainly not present in the ferritic matrix. Therefore, there is no definite base to disregard a possible effect of the presence of carbides on the embrittlement. The ferrite, on the other hand, cannot be considered to be an embrittlement resistant phase, since even though ferritic matrices have been found not to be susceptible to embrittlement, all other embrittled matrices have large amounts of ferrite. Another factor that could have an effect is the amount of interface in the matrix microstructure. Interfaces are favourable paths for diffusion and are also highly reactive sites. Ausferritic and pearlitic matrices, that are very susceptible to embrittlement, both have a large amount of interface area. Low tempering temperature martensites show incomplete recrystallization of ferrite and carbides, and also have a large amount of interface area. On the other hand, ferritic matrix microstructures only show the ferrite-ferrite grain boundary and ferrite-graphite interfaces. The smaller contribution of preferential diffusion paths, or the lower matrix reactivity could then be preventing the embrittlement of the ferritic matrix.

Table 2 summarises the results of all tensile tests carried out.

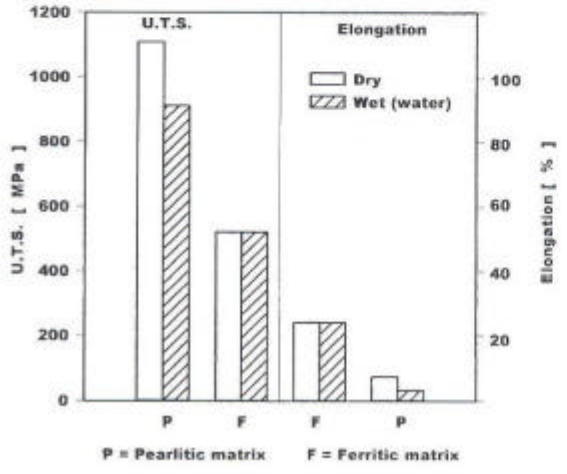

Fig. 8 U.T.S and elongation of other microstructures tested in water

Scanning microscopy results

The typical fracture surface of ADI tested under tension in dry condition is shown in Figure 9. The surface shows graphite spheroids (dark), voids left by graphite spheroids that remained attached to the complementary fracture surface (pointed by the arrow) and regions of ductile fracture, characterised by dimples. Small regions of cleavage facets are also present in some fields. Figure 10 shows areas of water tested samples of fully ductile fracture, while Figure 11 shows a predominant cleavage fracture in

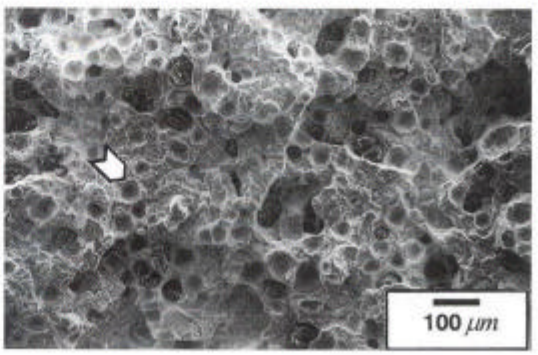

Fig. 9 Typical fracture in dry conditions

Table 2 Summary of measured tensile properties

Material	Mech. Prop.	Dry	Water	PH 5.51	PH 8.51	PH 11.91	Oil	Alcohol	WD40™
ADI	U.T.S [Mpa]	1168	852	844	854	871	1050	994	1165
Grade 2	δ [%]	16.0	2.80	2.4	2.1	2.6	8.5	5.3	16.0
ADI	U.T.S [Mpa]	1340	1030	–	–	–	1320	–	–
Grade 3	δ [%]	11.3	3.0	–	–	–	7.9	–	–
ADI	U.T.S [Mpa]	1526	1071	–	–	–	1456	–	–
Grade 4	δ [%]	6.3	1.2	–	–	–	4.5	–	–
Ferritic	U.T.S [Mpa]	517	516	–	–	–	–	–	–
matrix	δ [%]	25	26	–	–	–	–	–	–
Pearlitic	U.T.S [Mpa]	1100	900	–	–	–	–	–	–
matrix	δ [%]	7.3	3.1	–	–	–	–	–	–

a water tested sample. A more detailed examination of the water tested samples shows adjacent areas of ductile and cleavage fractures. This characteristic was already anticipated by Komatsu and co-workers[5]. The fracture surface of samples tested in contact with water and alcohol, show, in average, a larger proportion of cleavage facets than the fracture surface of samples tested in air. Nevertheless the change in the fracture behaviour is not general to all the fracture surface. The results suggest that the brittle behaviour is accompanied by a change in the fracture mechanism, although this change is not drastic. Areas of ductile, cleavage and mixed fracture can be found in all specimens. The main difference among samples is that the more embrittled the material, the larger the area of cleavage fracture surface. The distribution of the cleavage regions on the fracture surface takes place following patterns that are always in contact with the sample perimeter, as shown schematically in Figure 12. Unfortunately, a careful quantitative measurement of the fraction of cleaved fracture and a mapping of its distribution could not be carried out at this time, due to experimental limitations. Relatively large flat regions located near the perimeter are observed on the fracture surface of most embrittled samples, as shown schematically in Figure 12. This has been also reported by Komatsu *et al.*[5] Figure 13 a and b show the fracture surface of samples tested in oil and alcohol, where similar flat regions are observed in both specimens. Nevertheless, the nature of such flat portion of the fracture surface is different in each case. The flat portions found in water tested samples are characterised by cleavage planes, as shown in Figure 14, while dry tested samples show a different fracture type, as shown in Figure 15.

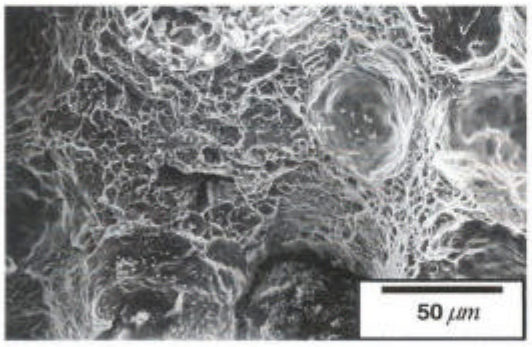

Fig. 10 Area of water tested samples with fully ductile fracture

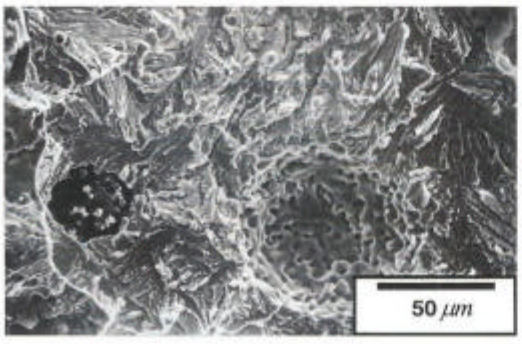

Fig. 11 Area of water tested sample showing predominant cleavage zones

The observation of some regions characterised by cleavage fracture near the surface of the sample suggests that a number of superficial cracks could have been growing along the tensile sample surface during testing. If so, other cracks may be visible on the lateral surface of the remaining parts of the broken specimens. This was examined by SEM on samples finely polished before testing. Samples tested under water only showed some small cracks growing on a plane perpendicular to the

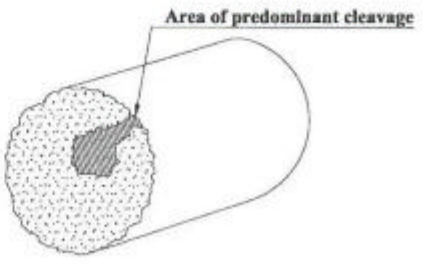

Fig. 12 Schematic representation of the distribution of predominant cleavage fracture areas on the tensile testing fracture surface

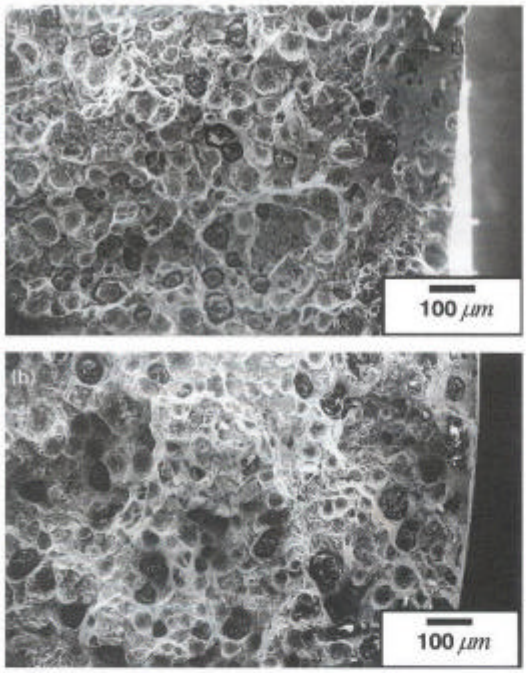

Figure 13 (a) Sample tested in oil. (b) Sample tested in alcohol

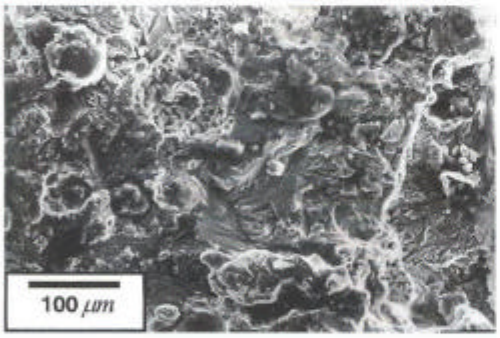

Fig. 14 Flat portions found in water tested samples (cleavage)

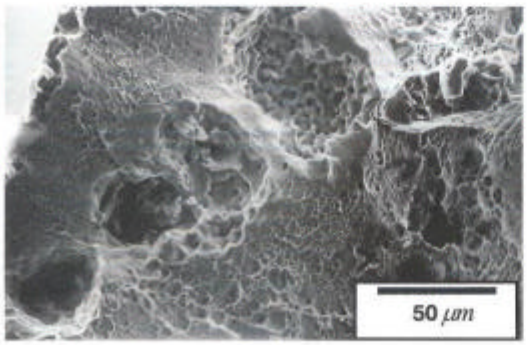

Fig. 15 Flat portions found in samples tested in air

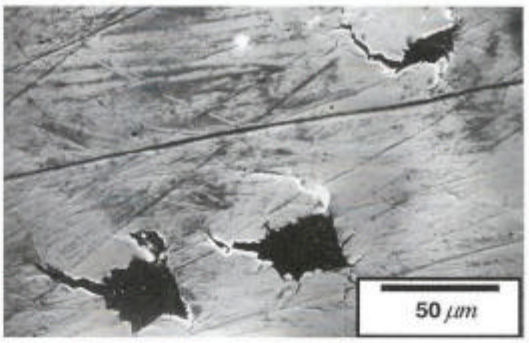

Fig. 16 Cracks observed in a side view of water tested specimen ($\delta = 2.85\%$)

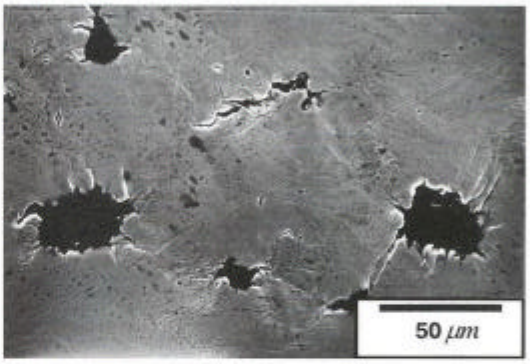

Fig. 17 Cracks observed in a side view of dry tested specimen ($\delta = 16\%$)

sample's axis, initiated at the graphite nodules, as shown in Figure 16. Some cracking was also observed on the samples tested in air, which produced a greater elongation (Figure 17). It is believed that some cracking appears after extensive plastic deformation in dry tested samples, and a more noticeable cracking is seen on water embrittled samples. Nevertheless, no large cracks bridging regions between nodules, were found along the surface of water tested samples.

Final remarks

Komatsu *et al.*[5] proved that the embrittlement of ADI can be avoided by painting or by creating a surface layer of ferrite on ADI parts. The later method is certainly not recommended for high performance ADI parts, since a layer of ferrite at the surface would decrease its hardness, making impracticable the use of high surface loads, and providing preferential sites for the nucleation of fatigue cracks.

Several liquids were found to cause embrittlement of ADI to some extent. The effects have been quantified. Nevertheless, the phenomenon is far from explained.

Conclusions

- The embrittlement effect found by Komatsu *et al.*, and Shibutani *et al.* has been verified in an independent laboratory and using a different base ductile iron.

- A noticable decrease in UTS and elongation takes place when ADI samples of grades 2 to 4 are tested immersed in water.
- Embrittlement is not affected by the concentration of protons in water, since similar results were obtained when testing in water based solutions pH ranging from 5.5 to 11.9.
- Embrittlement was also found when testing in contact with isopropyl alcohol and SAE 30 lubricant oil.
- A very strong wetting agent (WD40^{TM} oil) does not cause embrittlement.
- The phenomenon does not increase when the strain rate during testing is decreased.
- The pearlitic ductile irons suffer embrittlement in contact with water.
- Ferritic matrix ductile irons do not duffer embrittlement by contact with water.
- The present study advances the understanding of embrittlement in ADI materials, and identifies new embrittling liquids, but does not provide a definite explanation for its causes.

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