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Liquid metal embrittlement of an austenitic 316L type and a ferritic–martensitic T91 type steel by mercury

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Abstract

The susceptibility to liquid metal embrittlement (LME) of 316L and T91 steels by mercury has been studied at room temperature. A dedicated experimental device using center crack tension (CCT) specimens was built. We developed a specimen preparation procedure that must be rigorously applied in order to investigate the embrittling effect of Hg. The high strength ferritic–martensitic steel of type T91 is embrittled by Hg at room temperature over a large range of crosshead speeds, between 6.67×10^{-7} and 6.67×10^{-3} m s^{-1}. More surprisingly, the austenitic steel of type 316L is also embrittled by Hg between 1.67×10^{-8} and 2.5×10^{-4} m s^{-1}. The fracture of the T91 and 316L CCT specimens in contact with Hg occurs by shear band decohesion over the above-mentioned range of crosshead speeds.

1. Introduction

In this paper the question of the susceptibility to embrittlement of both ferritic–martensitic (of type T91) and austenitic (of type 316L) steels by mercury (Hg) at room temperature is briefly addressed. This study has two major motivations. One is related to the R&D for large installations since the 316L/Hg couple has been chosen for the US and Japanese spallation sources [1,2]. The other is directly related to the basic aspects of the phenomenon of Liquid Metal Embrittlement (LME). Indeed, Hg is a well-known embrittler of a number of solid metals and metallic alloys, with a notable exception: Fe/Hg is not *a priori* an embrittling couple. This was mentioned by Shunk in 1974 [3], repeated by Nicholas in 1981 [4] as a general statement suffering some exceptions.

LME refers to the degradation of the mechanical properties (generally tensile) of a stressed material, whilst in intimate contact (or wetting) with some liquid metal. The two main phenomenological criteria of occurrence of LME are good wetting and sufficient plastic deformation. Thus, we have to face the difficulty of how to wet a naturally oxidized steel surface with Hg. Indeed, oxygen is hardly soluble in Hg at room temperature, if one compares it with Lead alloys. The critical surface tension (CST) is the value of surface tension (ST) of a liquid below which the liquid will spread on a solid; the CST of the oxidized steel surface is low (in the order of 150 mN/m or less) compared with the ST of Hg ($435 \leqslant \gamma_{Hg} \leqslant 485$ mN/m). We immediately see that it is very difficult to wet either 316L or T91 with Hg. This was the subject of a preliminary work [5]. There is also the possibility to deposit the embrittling species by physical vapor deposition onto the steel surface after cleaning by Argon ion sputtering. This was done in a previous work, but it is difficult to extend this technique to large geometries [6].

Last, since we are also interested by the dynamics of crack growth under the influence of Hg, we have adapted the specimen geometry and used center crack tension (CCT) specimens. That will allow to follow the dynamics of fracture, which will be the topic of a forth coming paper.

To our knowledge, neither 316L nor T91, in standard metallurgical condition, was reported to be embrittled by Hg during constant deformation rate tensile testing [7,8]. In dynamic loading conditions (cyclic fatigue testing), an LME effect of Hg on 316L was reported, as a result of

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Table 1
Steels Composition (wt%, balance Fe)

Steel	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	Nb	Ti	V
316L	0.0185	0.67	1.81	0.032	0.0035	16.73	2.05	9.97	0.0183	0.23	–	0.0058	0.07
T91	0.1025	0.22	0.38	0.021	0.0004	8.99	0.89	0.11	0.0146	0.06	0.06	0.0034	0.21

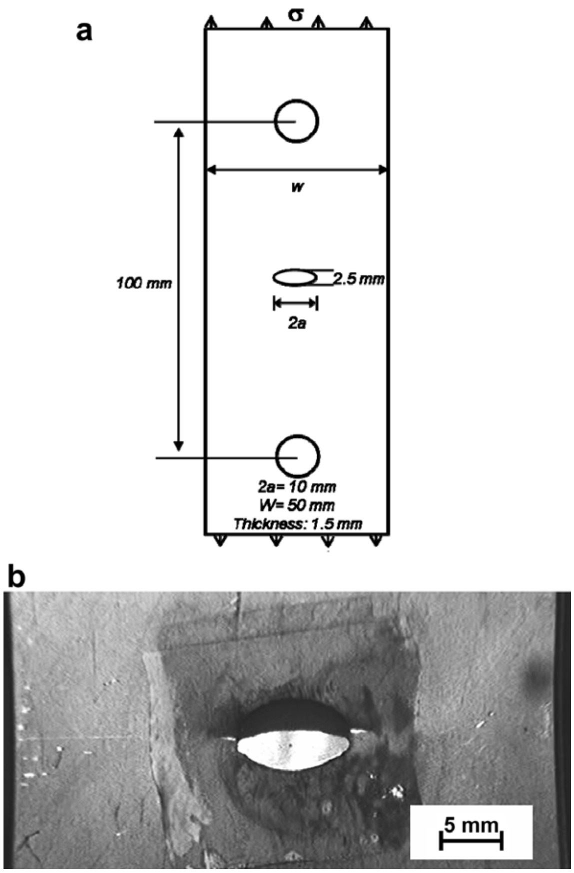

Fig. 1. (a) Center crack tension (CCT) specimen with dimensions (150 mm × 50 mm × 1.5 mm); (b) deformed notch with cracks nucleated at both sides, Hg is supplied at the crack tip by capillarity.

the studies carried out at Oak Ridge in the framework of the SNS spallation source project [9–11].

In this paper, by means of mechanical tests under constant crosshead speed using CCT specimens, first we show that not only the high strength steel, T91, is embrittled by Hg at room temperature, but also that an exemplary ductile structural material of fcc structure, like the 316L stainless steel, is also embrittled by Hg. More precisely, we shall see that LME manifests itself as a reduction in fracture strength and ductility, with no change in yield stress, which is precisely the definition of LME proposed by Gordon [12].

2. Experimental

The composition of the T91 and AISI316L steels are reported in Table 1. They are used in the standard metallurgical state (for T91 steel: austenitisation at 1050 °C and tempering at 750 °C; for AISI 316L SS: annealing at 1050 °C).

The CCT specimen, represented in Fig. 1(a) has a dimension of 150 mm × 50mm × 1.5 mm. The dimensions of the notch (outer dimensions: 2.5 mm × 10 mm, with 1.5 mm thickness) are chosen so that it can be used as a reservoir for the liquid metal, under the action of the capillarity forces. The specimen surface and inner sides of the notch are carefully hand polished with SiC paper down to grade 4000, then ultrasonically cleaned in absolute ethanol and air dried.

For T91, after mechanical polishing, the notch is immediately filled with Hg. Good contact is obtained after 48 h

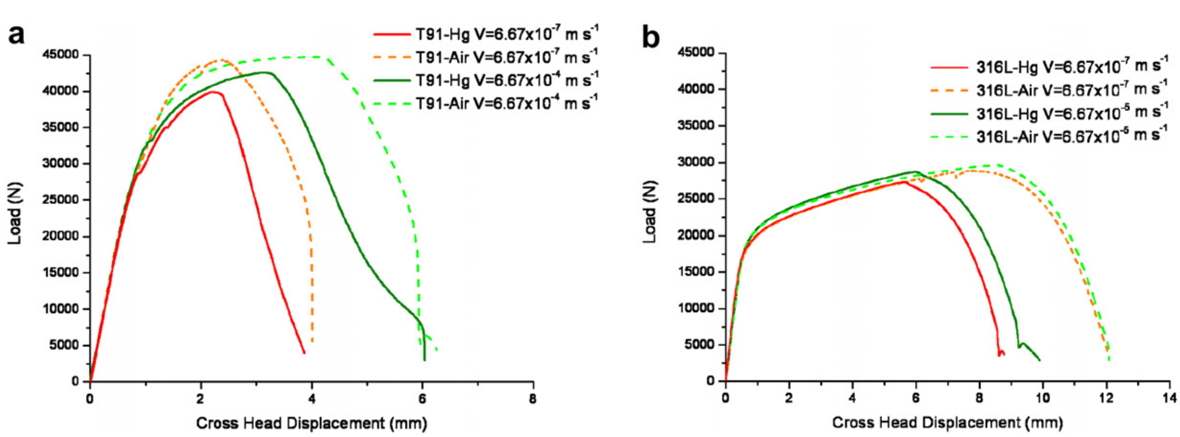

Fig. 2. Load versus cross head displacement curves obtained with CCT specimens at two crosshead speeds in Hg and in air: (a) T91 and (b) 316L. In both cases, an embrittling effect of Hg is visible at room temperature.

ageing: the notch walls are wetted with Hg. For 316L, the mechanical polishing is followed by chemical etching, using a 4% HCl aqueous solution; Hg replaces progressively the chloride solution and spreads onto the notch walls. As a result of a previous work, the two above-mentioned specific procedures were, respectively, established in order to wet the T91 and the 316L steel notches with Hg [5].

The CCT specimens with Hg filled notches are carefully inserted into the testing device adapted to a MTS 20/MH electromechanical tensile machine and then loaded at constant crosshead speed, varying between 1.67×10^{-8} and $2.5 \times 10^{-4}\ \mathrm{m\ s^{-1}}$ for 316L and 6.67×10^{-7} and $6.67 \times 10^{-3}\ \mathrm{m\ s^{-1}}$ for T91, knowing that the LME effects (width and depth of ductility trough...) are largely strain rate dependent [13,14].

In both cases (316L and T91), the notch part of the CCT specimen is maintained in between two transparent Plexiglas foils, which allows us to keep the Hg in the notch area during the whole period of preparation of the tensile test. Indeed, as soon as a crack is nucleated, Hg is supplied by capillarity at the crack tip (Fig. 1(b)).

3. Results and discussion

The load versus displacement curves are reported in Fig. 2 for both T91 and 316L in contact with Hg and compared with air reference curves. For an easier observation, only the curves corresponding to two different crosshead speeds are shown. There is no clearly observable effect of Hg on the yield stress in the present testing conditions (Fig. 2).

For both T91/Hg and 316L/Hg couples, a significant plastic deformation takes place before crack initiation, largely dependent on the applied crosshead speed. However, the presence of Hg reduces the amount of plastic deformation prior to cracking. This is clearly visible in Fig. 3, where the ruptured CCT specimens in contact with Hg are presented and compared to the air reference specimens. The onset of crack initiation is apparently varying with the crosshead speed. One can already note that the level of deformation required for crack initiation is reduced at lower crosshead speed. This observation is valid for both T91 and 316L independently of their respective structure and microstructure (Fig. 2).

Once initiated, the crack advance is progressive, until final rupture, and, in all cases, propagation proceeds because of the applied mechanical strain. In the present case, the crack spends its all life in a sub critical stage.

For both T91/Hg and 316L/Hg couples, the main features of the fracture surfaces are, respectively, represented

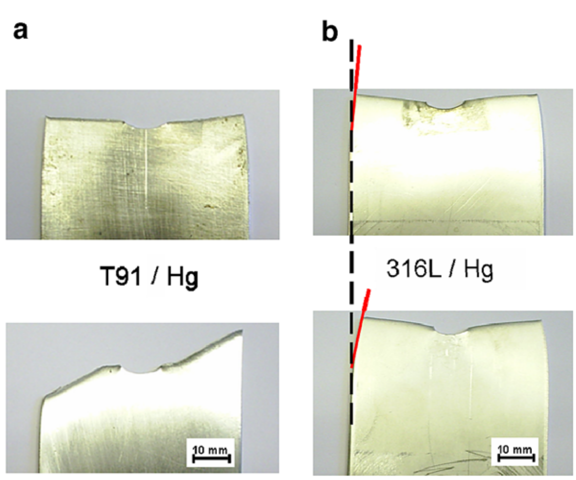

Fig. 3. Fractured specimens of 316L and T91 loaded at $6.67 \times 10^{-6}\ \mathrm{m\ s^{-1}}$, showing that the macroscopic deformation is significantly reduced in the presence of Hg for both T91 (a) and 316L (b) steels, independently of their structure and microstructure.

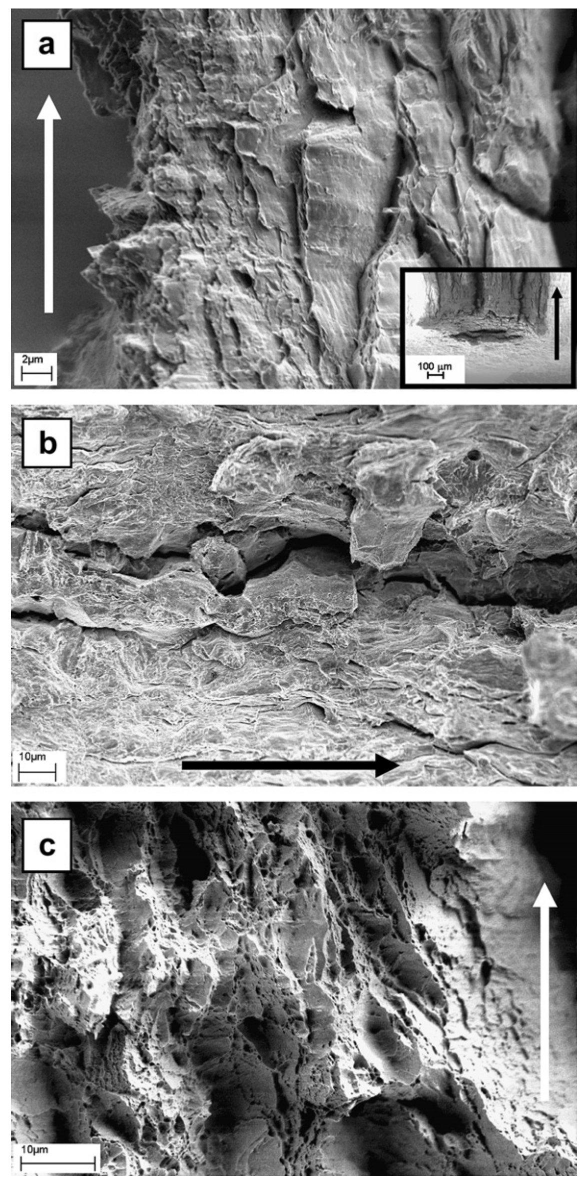

Fig. 4. SEM micrographs showing the fracture surface of T91 CCT specimens tested at $6.67 \times 10^{-6}\ \mathrm{m\ s^{-1}}$: (a) transgranular by shear band decohesion in Hg, (b) intergranular in Hg, (c) dimpled in air. The crack initiation zone is given in insert of (a) at lower magnification. The arrow indicates the direction of crack propagation.

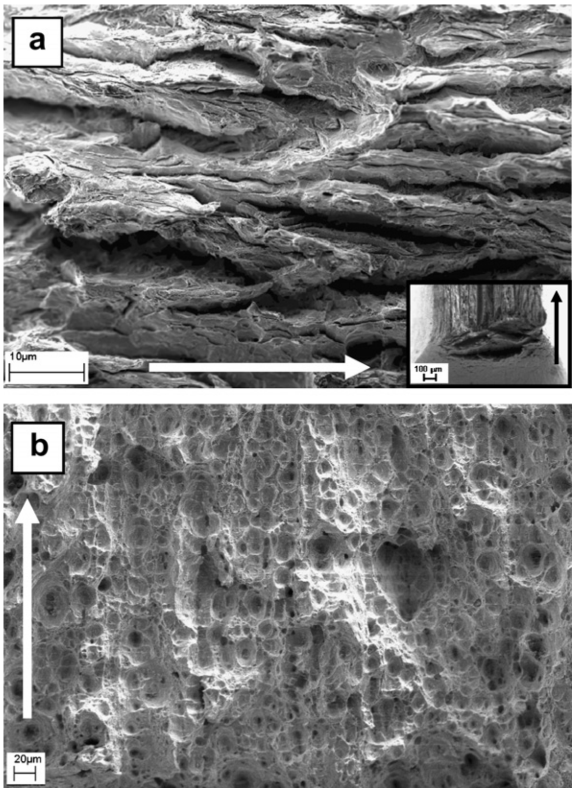

Fig. 5. SEM micrographs showing the transgranular fracture surface of 316L CCT specimens tested at 6.67×10^{-7} m s^{-1}: by shear band decohesion in Hg (a), dimpled in air (b). The crack initiation zone is given in insert of (a) at lower magnification. The arrow indicates the direction of crack propagation.

in Figs. 4 and 5, and compared to air reference specimens ruptured under similar testing conditions. It is noticeable that apparently the same fracture mechanism operates for T91/Hg and 316L/Hg, irrespective of the crystallographic and metallurgical features.

Fig. 4(a) shows two micrographs taken on the tested T91 steel at two different magnifications. The micrograph at lower magnification shows a multiple crack initiation, britte, in mixed mode I and II. Well-opened cracks that immediately started to propagate deeply inside the material are also visible in the crack initiation zone. At larger magnification, well-defined steps (in the range of 50–100 nm) are visible in this zone. Fig. 5(a) shows the crack initiation zone for the 316L/Hg couple at two magnifications and similar considerations as for Fig. 4(a) can be made.

For both T91 and 316L steels, the main crack propagates in the symmetry plane of the specimen, perpendicularly to the loading axis (Figs. 4(a) and 5(a)). There is no evidence of fracture by cleavage over the entire fracture surface. In the general case, there is no indication that the grain boundaries or any other micro-structural feature affects the crack propagation and branching in presence of Hg. However, some areas of mixed intergranular and transgranular fracture are visible for the T91/Hg couple (Fig. 4(b)).

Most fracture surface aspects show that fracture occurs by shear band decohesion, which is consistent with a plane stress shear deformation at 45° off the loading axis. The presence of Hg modifies the plastic deformation of the material (T91, 316L), and inhibits the fracture mode by nucleation – coalescence of voids, which would give rise to the dimpled fracture surface as observed in air (Fig. 4(c) for T91 and Fig. 5(b) for 316L). The above analysis is valid for all crosshead speeds considered in the present work.

To summarize the above findings, the present mechanical testing conditions, making use of carefully prepared CCT specimens whose notches are filled and wetted with Hg, are suitable to evidence the susceptibility to LME of both T91/Hg and 316L/Hg couples. To our knowledge, this is the first time that a shear band decohesion mode is identified as the operating fracture mode in LME.

4. Conclusions

The susceptibility to LME of two structural materials, namely a ferritic–martensitic of type T91 steel and an austenitic of type 316L steel in contact with Hg, was studied. The following points are worth mentioning:

- A specific device using CCT specimens was preferred. Special care was paid to the specimen preparation in order to optimize the contact conditions of Hg with the notch walls.
- The T91 steel is found embrittled by Hg over the whole range of crosshead speeds tested, between 6.67×10^{-7} and 6.67×10^{-3}. Two fracture modes are identified: transgranular fracture by shear band decohesion and, in some areas, intergranular fracture.
- The 316L austenitic steel is also found embrittled by Hg, as a result of the continuous loading tests performed between 1.67×10^{-8} and 2.5×10^{-4} m s^{-1}. Fracture occurs by shear band decohesion in all cases. To our knowledge, this could be the first manifestation of LME observed with the 316L/Hg couple under monotonous loading conditions, since the embrittling effect of Hg on a 316L stainless steel was until now solely observed during fatigue testing.
- For the first time, a shear band decohesion mode is identified as the operating fracture mode in LME.

In a future work, we will continue to investigate the influence of the strain rate on the fracture behavior. The aim could be to distinguish, if possible, a different response between T91/Hg and 316L/Hg.

Acknowledgments

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