Optimization of contact conditions between iron base alloys and mercury at room temperature

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Abstract

The intimate contact or wetting of iron-base alloys by mercury is obtained at room temperature by varying the environmental conditions, quasi immediately for Armco iron and a high purity Fe–25Ni alloy, after ∼30 min of contact for the 316L/Hg couple, after one week of contact for the T91/Hg couple. Careful mechanical polishing allows for wetting the notches of CCT specimens made in T91 steel with Hg, whereas chemical etching in 4%HCl is required to wet 316L SS identical specimens. Using ICP-OES measurements, values of solubility limit are given for both Fe (45.5 ± 0.4 wt ppm) and Cr (0.56 ± 0.07 wt ppm) in mercury at room temperature, the one of nickel (2.6 ± 0.39 wt ppm) being in agreement with the literature data.
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1. Introduction

Our general interest is the study of the susceptibility to embrittlement of chromium containing steels, namely, ferritic/martensitic (of T91 type) and austenitic (of 316L type) stainless steels, by mercury at room temperature. The objective of this paper is to optimize the contact conditions between the solid and liquid metal (LM) phases, which is one of the prerequisites of occurrence of liquid metal embrittlement (LME) [1].

After Kamdar [1], LME may happen when an oxide-free solid surface under stress is in contact with a certain LM phase. When dealing with naturally passive steel surfaces, it is crucial to obtain the required 'intimate contact' or wetting conditions, using Kamdar's terminology, before starting the LME study.

Moreover, a specific geometry is chosen, using center-crack in tension (CCT) specimens, to determine how mercury affects crack propagation. Thus, we concentrate on the contact conditions between mercury filling the notch and the notch walls of CCT steel specimens. Optical and SEM observations of CCT specimens associated with a chemical analysis of mercury filling the notches of the CCT specimens are used to characterize and optimize the steel/Hg contact conditions.

Little is known about the contact with mercury of quasi – insoluble metals, like iron, nickel, manganese [2] and especially chromium, their solubility in Hg varying by orders of magnitude depending on the author [3–7]. It is sometimes stated that a very limited amount of solubility in the LM facilitates 'intimate contact' or wetting, but that LME rarely occurs in S/L metal systems exhibiting a significant mutual solubility [1].

For the T91/Hg couple, to our knowledge, information on wetting at room temperature is missing. On the contrary, for the 316L/Hg couple, there are studies concerning the influence of mercury on the fatigue and corrosion behavior of 316L [8–22], which is the S/L couple of both Japanese and American spallation targets [23,24].

Studies of wetting of stainless steels and nickel-based alloys by mercury have shown that they were unwetted by mercury at or near room temperature, when the samples were exposed to mercury in air for 72 h, and that there was no discernible wetting until 225 °C even when the material surface was gold-plated or cleaned with acid [8,10,15]. On

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the other hand, the fracture surfaces of 316LN SS, after fatigue testing in mercury at room temperature, were found completely wetted by mercury [9]. Moreover, 316L SS samples under cavitation conditions with acoustic pressure waves of frequency 20 kHz and 1.5 MPa of amplitude resulted in apparent wetting by mercury at room temperature in only 24 h [13]. These results show the important role of the native oxide in the wetting behavior. They also reveal that 316LN SS fresh surfaces may be wetted by mercury at room temperature. To our knowledge, in the studies dealing with wetting by Hg at room temperature, an indirect method is employed, for example making use of zinc amalgams as an intermediate stage [8,25].

In this paper, we focus on the contact conditions between the T91 martensitic steel and mercury, a priori hindered by an interfacial oxide, by comparison with the rather good contact with Hg obtained in the case of austenitic steels (316L and 304), Armco iron and high purity iron–nickel alloys. Different wetting methods for the CCT specimens of both austenitic (316L) and martensitic (T91) steels are presented. The relation between wettability and solubility is discussed. Finally the more adapted treatments of the CCT specimens to follow the crack propagation under the influence of mercury are chosen.

2. Experimental

The compositions of the steels used in this work, T91 and 316L, are reported in Table 1. The main impurities in Hg (PROLABO) are the following: Al: 30 wt ppm; Ba: 2 wt ppm; Cr: <0.2 wt ppm; Cu: 11 wt ppm; K: 11 wt ppm; Mg: 14 wt ppm; Mn: 0.9 wt ppm; Mo: 1 wt ppm; Na: 12 wt ppm; S: 54 wt ppm; Sr: 0.7 wt ppm; Zn: 23 wt ppm.

Starting with (150 × 50 × 1.5 mm) platelets of T91 and 316L, CCT specimens, usually used for toughness testing, are machined by electro-erosion. An elliptical notch of 10 mm in length, 2.5 mm width, with walls of 1.5 mm thickness is obtained. One sample, half filled with mercury, is shown in Fig. 1.

To fill the notch with mercury and wet the notch walls of the specimens, five preparation procedures are tested:

(1) Mechanical polishing of the specimen surface and notch walls using SiC papers to grade 4000, followed by ultrasonic cleaning in absolute ethanol and drying in air.
(2) Mechanical polishing followed by chemical etching, using concentrated hydrochloric acid (37%) for 5 min, rinsing in distilled water, followed by ultrasonic cleaning in absolute ethanol and drying in air.

Fig. 1. CCT specimen, with notch machined in a T91 steel plate, wetted by mercury (white in the picture).

(3) Mechanical polishing followed by chemical etching, in 4% hydrochloric acid for a few minutes. The acidic solution is progressively displaced by mercury on the steel surface.
(4) Electropolishing, using a mixture of 5% perchloric and 95% acetic acids at 35 V for 2 min [26].
(5) Electropolishing followed by chemical etching, as described in (2).

Then, the notches are immediately filled with a mercury drop using a syringe; when necessary, the mercury is pressed to force a macroscopic contact with the notch walls.

All these preparation procedures were tested with the T91 specimens. Only procedures (1) and (3) were applied to 316L specimens.

After varying the ageing periods (30 min, 2, 3, 5, 7, 14, 21 and 28 days), the samples are observed in an optical microscope. Then, the mercury is removed from the notch using a syringe and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) to detect the metallic elements, especially iron, chromium and nickel dissolved during the ageing period. The specimens are then observed and analyzed using a LEO 1530 FEG-SEM.

In ICP-OES, a constant flow of liquid sample is transported into a nebulizer where the liquid is converted into an aerosol. Then the aerosol is transported into the plasma where it is dissolved, vaporised, atomized, excited and/or ionized by the plasma. The excited atoms and ions emit characteristic radiations, which are collected and sorted by wavelength. Calibration curves relating the instrument response to the sample concentration are linear over a wide concentration range.

A specific ICP-OES analytical method is applied. The samples are dissolved in high purity HNO_3. ICP-OES measurements were carried out with a spectrometer Varian model Vista AX. The detection limit (DL) is defined as

Table 1
Chemical composition of 316L and T91 steels used in this work (wt%)

Steel	Fe	C	Si	Mn	P	Cr	Mo	Ni	Al	Cu	Nb	Ti	V	W	N
T91	Balance	0.1025	0.22	0.38	0.021	9.25	0.89	0.11	0.0146	0.06	0.06	0.0034	0.21	0.01	0.0442
316L	Balance	0.0185	0.67	1.81	0.032	16.73	2.05	9.97	0.0183	0.23	–	0.0058	0.07	0.02	0.0293

Table 2
ICP theoretical detection limit (DL) and quantification limit (QL) for chromium, iron and nickel in Hg with the present ICP-OES parameters given in Section 2

	Cr (µg/g)	Fe (µg/g)	Ni (µg/g)
DL	0.003	0.02	0.007
QL	0.007	0.06	0.015

the background signal plus three times the standard deviation of the background signal divided by the slope of the calibration curve. The quantification limit (QL) is defined as the background signal plus ten times the standard deviation of the background signal divided by the slope of the calibration curve. The optimums DL and QL are obtained using the following parameters of the plasma: Power = 1.5 kW; Auxiliary flow = 2.25 l/min; nebulizer flow: 0.7 l/min; replicate read time: 40 s; pump rate: 11 rpm. The samples concentration varies from 4 to 6 g/L. Three wavelengths per element are considered: 267.716 nm, 206.550 nm and 206.158 nm emission lines for Cr, 259.940 nm, 234.350 nm and 238.204 nm emission lines for Fe and 230.299 nm, 21.648 nm and 231.604 nm emission lines for Ni. In these conditions, the theoretical DL and QL for each element are presented in Table 2.

3. Results and discussion

3.1. Macroscopic wetting

Treatment (3) (Mechanical polishing followed by chemical etching in 4% hydrochloric acid) permits immediate spreading of Hg on platelets of Armco Iron and high purity Fe–25%Ni, whereas a few minutes of exposure to the acidic aqueous solution is necessary to obtain that some Hg droplets stick, enlarge and spread onto the type 304 and 316L SS surfaces (Fig. 2).

Simple mechanical polishing allows for wetting T91 steel by Hg (Fig. 1). Any other treatment (2–5) was found un-adapted. The mercury drops remaining on the T91 steel surface after injection with a syringe neither stick nor spread on the steel surface, whatever be the ageing time. It is suggested that the growing oxide destabilizes the poorly adherent Hg drops on T91. By nature, the oxide film on T91, initially the native oxide, $FeCr_2O_4$ [27], and the one growing progressively at room temperature in contact with hydrochloric aqueous acid solution, does not allow for wetting by mercury.

3.2. Optical observations

The study of the contact conditions between steel and mercury is continued by OM observations of the notch region filled with mercury, as a function of the preparation methods and ageing time (Figs. 3 and 4).
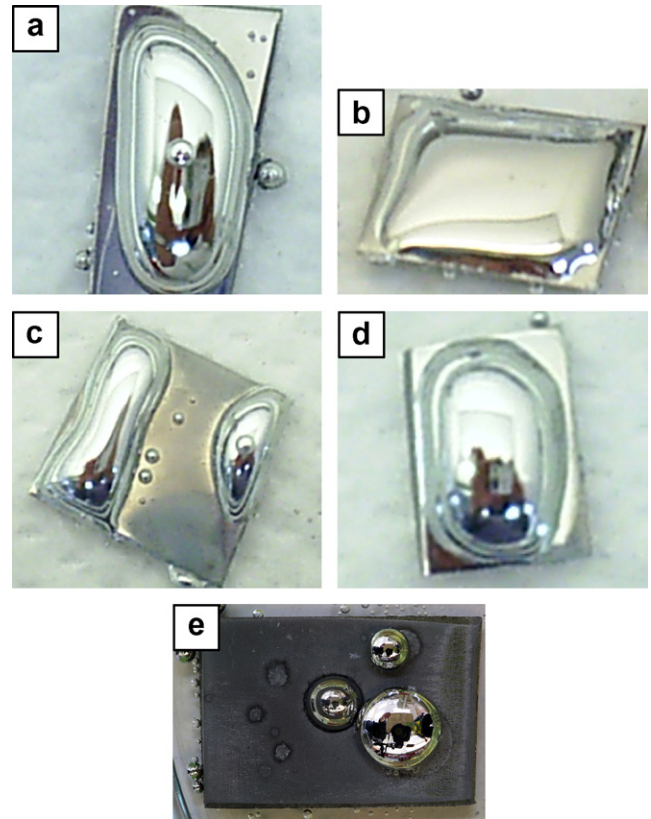

Fig. 2. Top view of various Iron alloys mechanically polished and immersed in 4%HCl aqueous solution, after injection of Hg onto the surface, at room temperature: (a) Armco iron and (b) high purity Fe–25%Ni alloy are immediately 'wetted' by mercury; (c) 304 and (d) 316L stainless steels are also 'wetted', the Hg drop spreading more efficiently after a few minutes of immersion of the Steel platelet in the acidic aqueous solution. To the contrary, for T91 steel (e) only very few drops stick to the surface after a few minutes of immersion of the T91 specimens in the acidic solution; both sticking and spreading are hardly visible after 5 days ageing, these effects being apparently counteracted by the surface oxidation of the T91 steel.

When 316L SS specimens are just mechanically polished (see (1) above), the contact with Hg is quasi nil in the tip zone and quite loose in all the other notch zones, immediately after injection of mercury (Fig. 3(a) and (b)), and even after one week ageing (Fig. 3(c) and (d)). Mechanical polishing followed by chemical etching in 4%HCl (see (3) above) improves significantly the contact with Hg, in the tip zone (Fig. 3(f)), in spite of heterogeneities of contact (Fig. 3(e)) observable everywhere in the notch.

Contrary to 316L SS, T91 steel cannot be wetted by mercury when the specimen preparation involves any final chemical or electrochemical treatment ((2)–(5) above). Mechanical polishing remains the more appropriate method to obtain the contact of Hg with the notch walls of the T91 steel specimens, with no ageing effect at the scale of one week (Fig. 4). The notch tip is filled by mercury, but the adherence of the mercury is variable depending on the notch walls regions (Fig. 4 right).
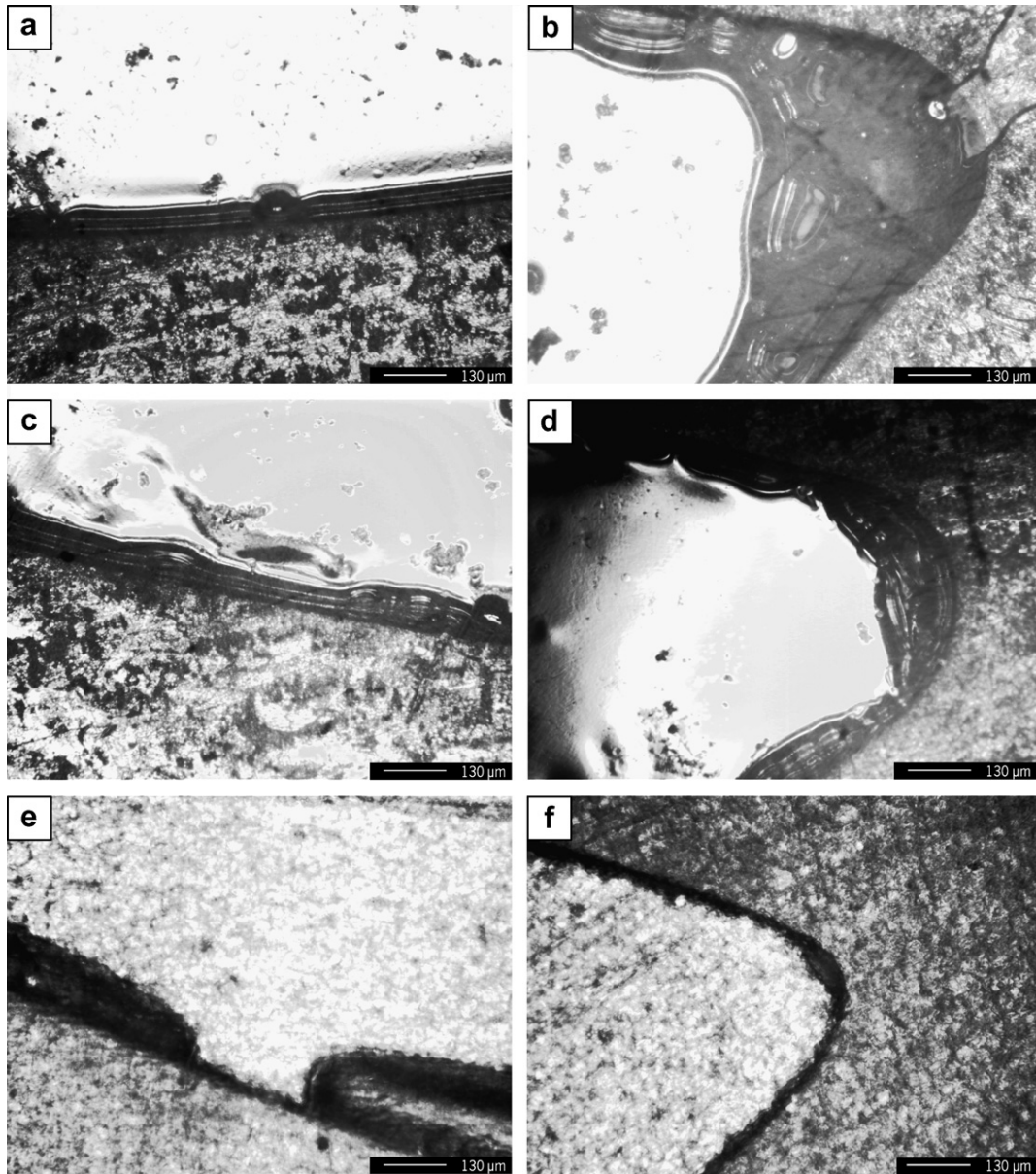
Fig. 3. Optical view of the notch machined in 316L stainless steel filled with mercury, in the region of lowest curvature (left) and at the tip (right): just mechanically polished immediately after injection of mercury (a and b) and after one week ageing (c and d), chemically etched in 4%HCl aqueous solution immediately after injection of mercury (e and f).
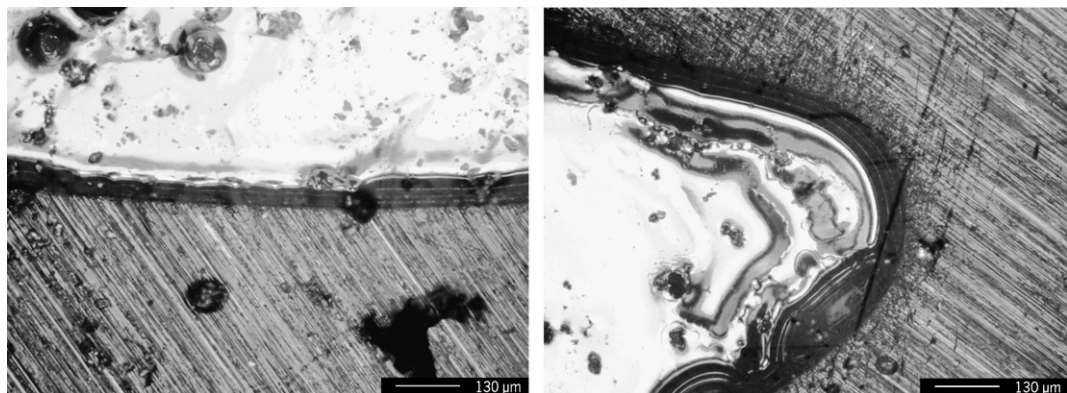

Fig. 4. Optical view of the notch machined in T91 steel filled with Hg, in the region of lowest curvature (left), at the tip (right). At this scale, no evolution of the contact with ageing time is detected between a few hours (this picture) and one week.

3.3. SEM observations

They are carried out after removal of Hg on 316L and T91 specimens for which the optimal contact with Hg was found by OM.

For mechanically polished T91 specimens, some mercury remains adherent onto the steel surface, taking the form of small mercury drops spread on the steel surface (Fig. 5(a)). In similar conditions, the tip of the notch is completely wetted by Hg (Fig. 5(b)), and a mercury layer is present on the entire notch walls (Fig. 5(c)). The presence of Hg is confirmed by EDX microanalysis (Fig. 5(d)).

For mechanically and electro-polished T91 specimens (method (4)), an oxide layer is observed on the notch walls (Fig. 5(e)). This oxide layer is partially detached by mercury during ageing (Fig. 5(e)–(h)). Some mercury drops on bared areas are also detected (Fig. 5(e) in BSE). This might indicate that stagnant Hg is not inert, but contributes to dissolve the superficial oxide.

In spite of the fact that the experimental conditions do not allow for contact angle measurements and determination of the wetting properties [2], it is suggested that at least partial wetting of T91 by Hg is attainable macroscopically (Fig. 5(a) and (b)).

Moreover, once the mechanically polished notches in the T91 platelets are filled with mercury, it was found very difficult to remove the mercury from the notch after one week ageing, Hg being strongly adherent to the notch walls.

For mechanically polished 316L SS specimens, SEM examination corroborates the above OM observations: not only the notch tip area does not contain even traces of mercury (Fig. 6(a)), but round-shaped Hg droplets are found on the 316L steel surface (Fig. 6(b)). Mechanical polishing is not suitable to wet 316L SS by mercury.

To the contrary, when the 316L SS specimens are chemically etched in 4%HCl after mechanical polishing, Hg spreads on the notch walls (Fig. 6(c)), fills the tip of the notch after 30 min of contact (Fig. 6(d)), while replacing the 4%HCl aqueous solution from the steel surface, as proved with Fig. 6(e) and (f): the surface is found smooth, with no chloride crystals (possibly of type $CrCl_3\ldots$) in the region where the Hg drop retracted (Fig. 6(f)), contamination by chloride crystals being just detected outside the drop (Fig. 6(g)).

It appears that chemical etching is convenient for wetting 316L SS by Hg at room temperature, and absolutely not for T91 steel in similar conditions, and to the opposite that mechanical polishing is suitable for wetting T91 steel by Hg, and not adapted for 316L SS.

3.4. Dissolution of iron and chromium in mercury at room temperature, as a function of ageing for both T91/Hg and 316L/Hg couples

ICP-OES was used to analyze the mercury removed from the notch of both the T91 and 316L SS specimens

(Fig. 1). In Fig. 7(a) and (b), the amounts of chromium and iron dissolved at room temperature in the mercury confined in notches formed in T91 steel platelets, as a function of the experiment duration and for all pre-treatments. In Fig. 8 are shown the amount of iron, nickel and chromium, respectively, dissolved in the mercury confined in notches formed in chemically etched (in 4%HCl) 316L SS platelets as a function of the experiment duration.

Apparent values of solubility limits at saturation, $x_{Me(Hg)}^{sat}$, with Me = Fe, Cr, Ni, will be derived from the data in Figs. 7 and 8. Indeed, the influence of non-metallic impurities, of amalgams and other intermetallic compounds formation is not taken into account. It could be the case only if we could prove that there is no interfacial barrier, of oxide type or not, which could limit the transfer of the alloying elements into the LM and retard the establishment of a steady state at the S/L interface.

Considering Fig. 7(a), chromium remains at or slightly above its detection limit (3×10^{-3} wt ppm), whatever the pretreatment ((2)–(5) above) during the first three weeks of confinement of Hg in the notch, with exception of the mechanically polished T91 specimens, for which Cr increases abruptly after three weeks ageing, reaching 0.56 ± 0.07 wt ppm.

Assuming $x_{Cr(Hg)}^{sat} \sim 0.56 \pm 0.07$ wt ppm, the amount of Cr measured in mercury after one more week of confinement in the notch should not vary significantly. The decrease by a factor 5 observed after one month (0.10 ± 0.04 wt ppm Cr) could be explained by the formation of insoluble compounds precipitating on the notch walls, concomitant with a slow re-oxidation of the notch walls due to the residual oxygen in Hg. To our knowledge, the solubility of oxygen in Hg is largely unknown, the only available information being related to the composition and crystallographic structure of some Hg oxides. However, in the case they form, the nature and stability of such compounds are unknown in the present experimental conditions [28].

For electro-polished T91 specimens, the detection of chromium in Hg is delayed, until one month ageing (Fig. 7(a)), which is consistent with the protective character of the oxide film produced by electropolishing.

These ICP-OES measurements allow for improving the characterization of the T91/Hg contact conditions. According to the SEM observations of Fig. 5(a)–(c) performed on mechanically polished specimens, the T91/Hg contact is established after one week. Using as a criterion the amount of Cr dissolved in Hg (Fig. 7(a)), we show that it takes at least three weeks to obtain a 'reactive wetting' of T91 by Hg.

Considering now Fig. 7(b), the following points are noticeable: (i) there is a delay before the beginning of substantial iron dissolution into Hg, considering both DL (0.02 wt ppm) and QL (0.06 wt ppm) for Fe in Hg at room temperature (Table 2); (ii) the delay is shorter for Iron (one week) than for chromium ($\geqslant 3$ weeks); (iii) the delay time is largely independent of the pretreatment; (iv) however, once
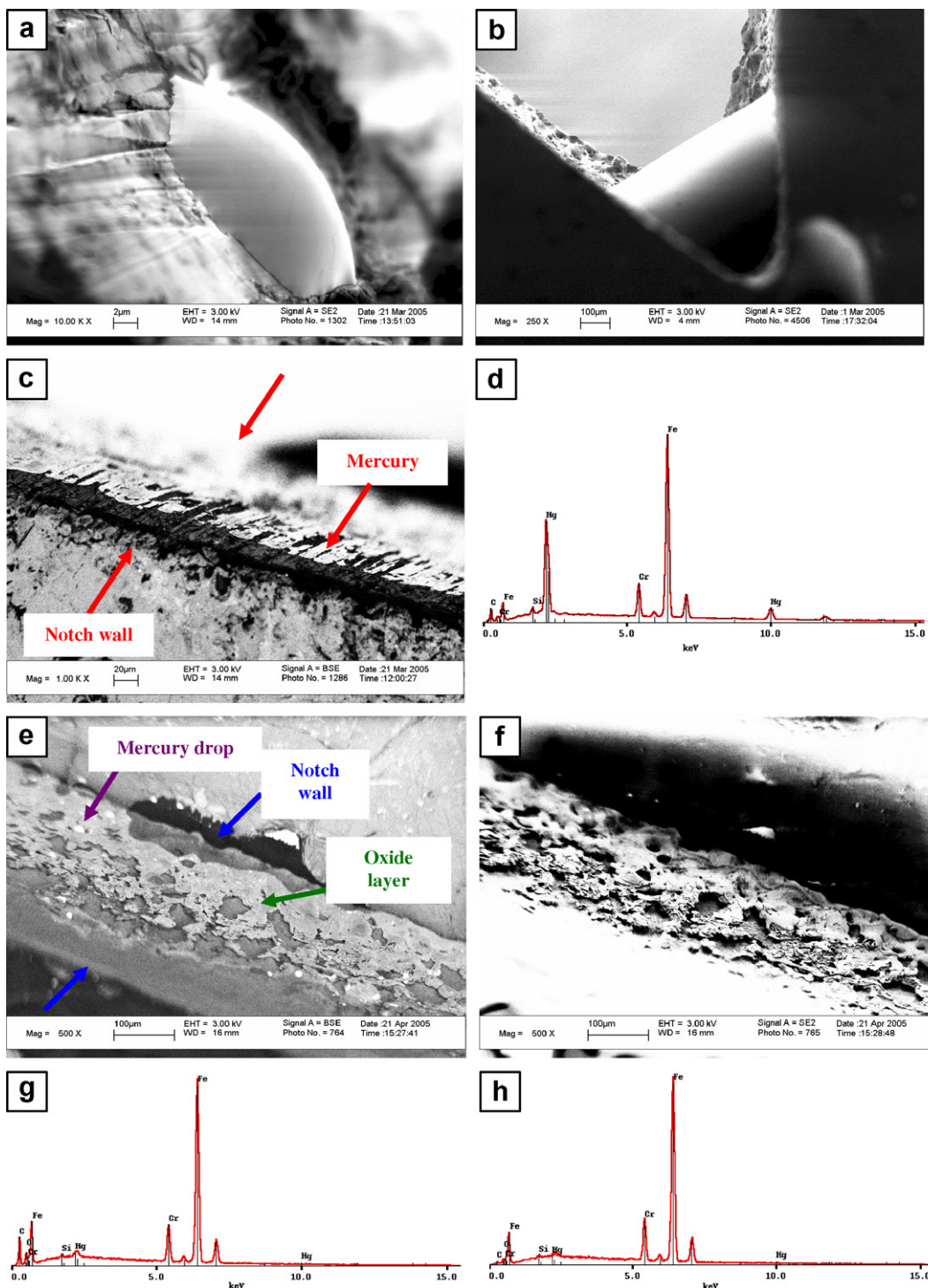
Fig. 5. SEM observations of the notch walls of a T91 steel CCT specimen, which was initially prepared by mechanical polishing, once removal of mercury out of the notch after one week ageing: (a) mercury drop on the T91 steel surface; (b) mercury filling the notch tip area; (c) mercury layers on the notch walls; (d) EDX Analysis of the corresponding mercury layers; note the quasi absence of carbon and oxygen. To the contrary, when the T91 CCT specimens were prepared by electropolishing, the following points are noticeable: (e) an oxide layer is observable on the notch walls, locally attacked after one week exposure to the LM at room temperature with a few Hg droplets in the regions where the oxide has been detached (BSE); (f) SE view of the notch walls; (g) EDX analysis of the oxide layers; note the presence of carbon and oxygen at 15 keV; (h) EDX analysis of the oxide-free zone, assumed to have been in direct contact with Hg and note the absence of carbon in comparable analytical conditions (15 keV).

dissolution begins, the amount of Fe dissolved is a function of the applied pretreatment to T91, suggesting that the interface controls the dissolution kinetics; (v) the plots of

dissolved Iron *vs.* exposure time to Hg pass through a maximum after two or three weeks, depending on the pretreatment, which is consistent with the presence of an interfacial
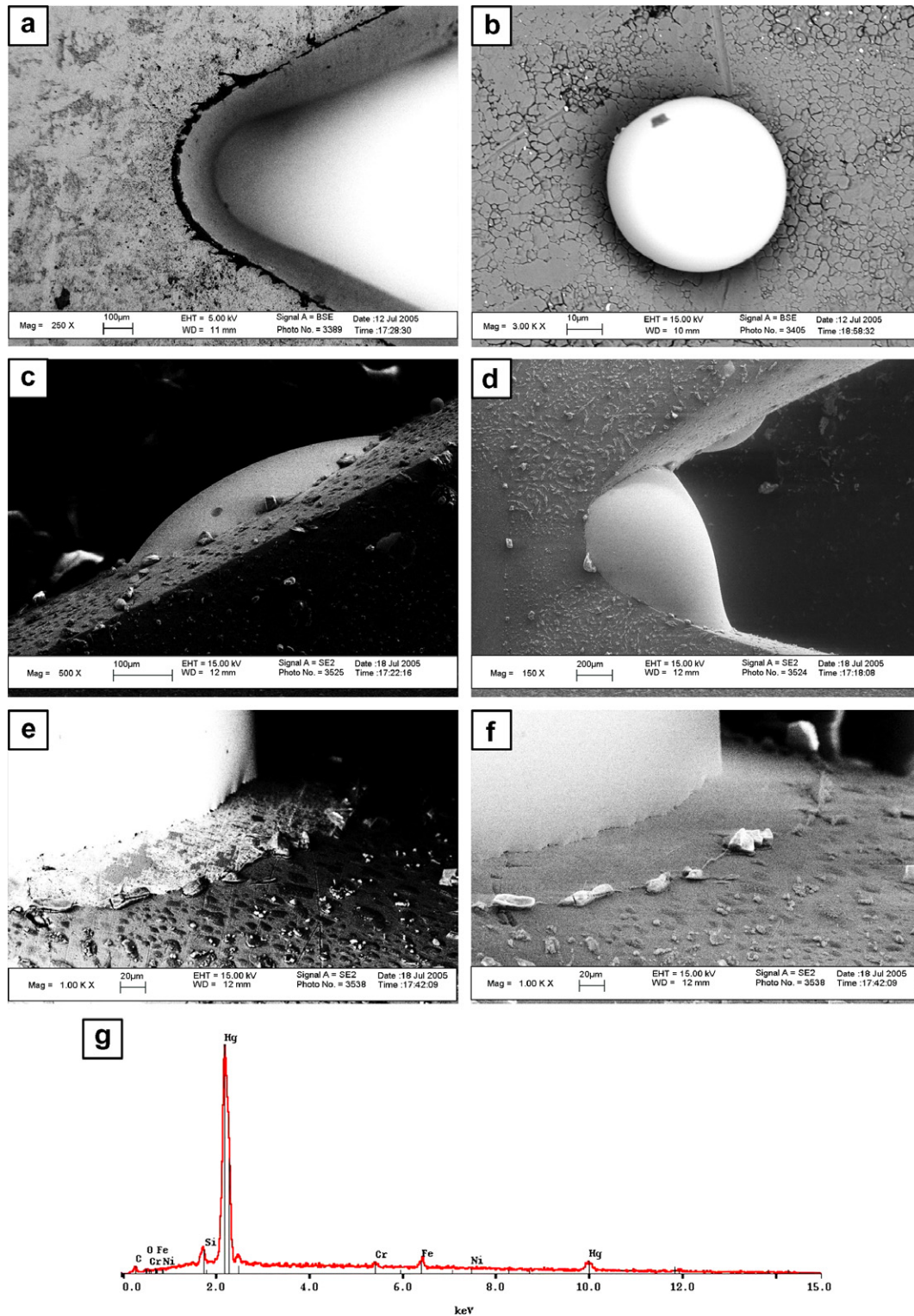
Fig. 6. SEM observations of the notch walls of a 316L SS CCT specimen after one week ageing (a and b) and after 30 min ageing (c–f) of the notch area filled with mercury, using two different preparation conditions. For initially mechanically polished specimens, we observe: (a) notch tip area non-wetted by Hg and (b) mercury round droplets onto 316L steel surface, i.e. no wetting by Hg. For chemically etched in 4%HCl specimens, we observe: (c) mercury drop spreading onto the 316L SS surface; (d) mercury filling the notch tip area; (e) mercury layers on the notch walls revealing that the mercury shifted from its initial place on the steel surface (BSE); (f) SE view of the smooth surface area initially covered by mercury, with chloride crystals at the periphery and (g) EDX analysis of the mercury layers, note the absence of Chlorine, which points to the total replacement of the acidic chloride solution by mercury in case of good 'wetting' of 316L SS by Hg (15 keV).
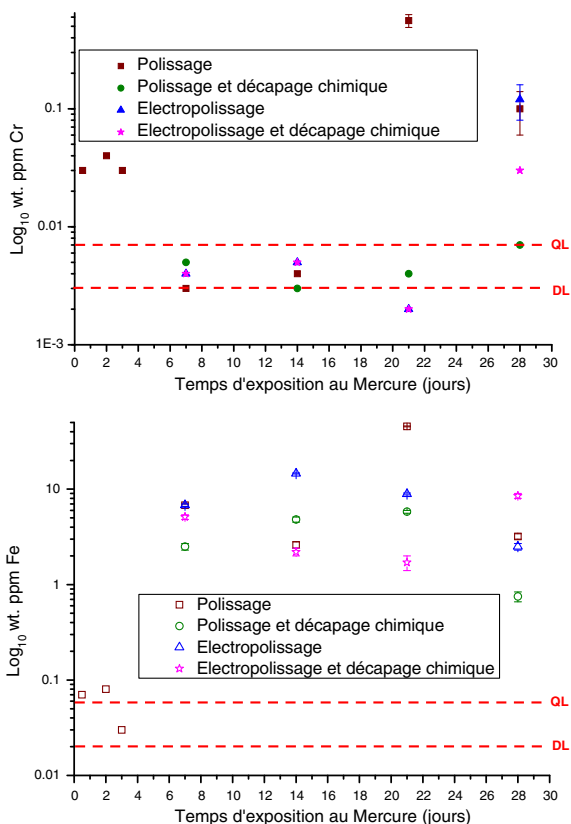
Fig. 7. Cr (a) and Fe (b) (in wt%) dissolved in mercury as a function of the contact time with the walls of the notch machined in the T91 steel. The various applied pre-treatments are indicated. The dashed lines represent the detection limits (DL) and quantification limit (QL) for Cr and Fe found by ICP-OES in Hg, in present experimental conditions.
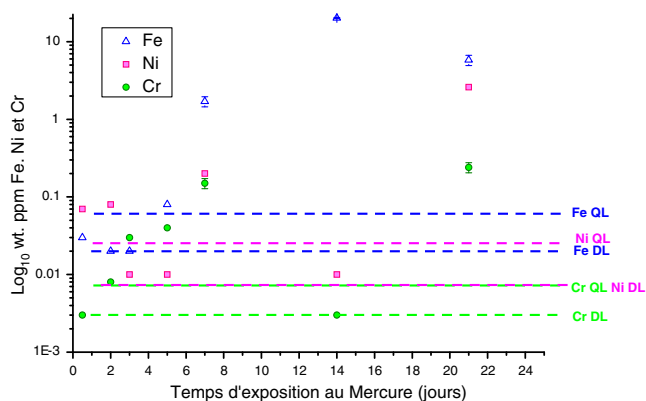

Fig. 8. Ni, Fe and Cr (in wt ppm) dissolved in mercury as a function of the contact time with 316L steel. The dashed lines represent the detection limits (DL) and quantification limit (QL) for Fe, Ni and Cr found by ICP-OES in Hg, in the present experimental conditions.

film whose properties vary with the pretreatment; (vi) whatever the pretreatment, it is apparently not possible to remove completely the interfacial film after one month ageing.

Here again, mechanical polishing seems to be the optimum treatment for T91 since the dissolved Iron after three weeks (45.5 ± 0.4 wt ppm) is between 5 and 10 times larger

than for any other pretreatment. As concerns the other pre-treatments, there is a factor of five between the extrema after three weeks: 8.9 ± 0.2 wt ppm Fe for electro-polished T91, 5.8 ± 0.2 wt ppm Fe for polished and chemically etched T91, and 1.7 ± 0.3 wt ppm for electro-polished and chemically etched T91. We propose the Fe solubility limit, $x^{sat}_{Fe(Hg)}$ reaches 45 ± 0.4 wt ppm in Hg at room temperature.

3.5. Dissolution of iron, chromium and nickel in mercury at room temperature, as a function of ageing for the 316L/Hg couple

We analyze the mercury confined in the notches machined in 316L SS platelets (Fig. 8): Ni is detected first, Cr after two days ageing, then Fe after five days ageing, referring to their respective DL and QL limits (Table 2). The plot of dissolved iron *vs.* exposure time to Hg passes through a maximum after two weeks (20.2 ± 0.3 wt ppm).

The influence of the exposure time to Hg seems more complex for Cr and Ni. The amount of dissolved Cr first increases with ageing up to one week, then decreases to the DL range (3×10^{-3} wt ppm) after two weeks, before rising again to 0.24 ± 0.036 wt ppm after three weeks. Likewise, the amount of dissolved Ni passes through successive maxima and minima with increasing exposure time to Hg. Nickel is immediately detected (Fig. 8). The detected amount of nickel never exceeds 2.6 ± 0.39 wt ppm. We assume $x^{sat}_{Ni(Hg)}$ attains 2.6 ± 0.39 wt ppm. This solubility value could be underestimated referring to the evolution of the amount of nickel dissolved in Hg with ageing time, shown in Fig. 8.

3.6. Comparison between the ICP-OES measurements in mercury as a function of the nature of the steel 'container': T91 or 316L

The following points are remarkable:

– The amount of dissolved chromium is found maximum after three weeks for both T91/Hg (0.56 ± 0.07 wt ppm) and 316L/Hg (0.24 ± 0.036 wt ppm) couples, thus by a factor of 2 higher for T91/Hg by comparison with 316L/Hg. In the latter case, it is very likely that a steady state is not yet attained after three weeks and that chromium should continue to dissolve in mercury with increasing ageing, until attainment of $x^{sat}_{Cr(Hg)} \sim 0.56$ wt ppm Cr as already mentioned above.
– The amount of dissolved iron attains its maximum (45.5 ± 0.4 wt ppm) after three weeks for T91/Hg, and apparently after two weeks (20.2 ± 0.3 wt ppm) for 316L/Hg. Considering Fig. 8, we suppose that once again, three weeks ageing is not enough to attain the above assumed solubility limit $x^{sat}_{Fe(Hg)} \sim 45$ wt ppm.
– The dissolution of nickel in mercury does not increase monotonously with ageing for 316L/Hg (Fig. 8), in spite of the fact that Ni dissolves quasi immediately into

Mercury, which would not be inconsistent with the existence of intermetallic compounds in the Hg–Ni thermodynamic equilibrium phase diagram [29], never mentioned for Fe [30] or Cr [31] in Hg.

– Consequently, the postulated solubility limit, $x_{Ni(Hg)}^{sat} \sim 2.6 \pm 0.39$ wt ppm found at room temperature, could be slightly underestimated.

3.7. Solubility limits of iron, chromium and nickel in mercury at room temperature

The experimentally determined solubility limits for Cr, Fe and Ni in mercury at room temperature, together with the corresponding available literature data, are, respectively, reported in Tables 3–5.

First, it is worth recalling that so long as the local composition and structure of liquid Hg in which Fe, Cr or Ni dissolve at room temperature is ignored, referring either to the formation of metal solute clusters, or to the formation of intermetallics compounds which may include non-metallic impurities, the solubility data must be considered cautiously. In fact, the announced solubility limits of the literature, $x_{Me(Hg)}^{sat}$, with Me = Fe, Cr or Ni, depend on the detection methods and their improvements during the twentieth century!

For example, there are large discrepancies between the values of $x_{Cr(Hg)}^{sat}$ reported in Table 3, in between 18 and 30 °C [3–5], going from 3.1×10^{-7} wt ppm for Tammann and Hinnüber [3] to 0.3 or 0.4 wt ppm according to de Wet and Haul [5], and even 1.3 wt ppm after Kozin [32]. The value of 1.92×10^{-3} wt ppm obtained by extrapolation of high temperatures data by Jangg and Palman [6] is certainly largely underestimated [33].

In this work, we propose $x_{Cr(Hg)}^{sat} \sim 0.56 \pm 0.07$ wt ppm at room temperature, in rather good agreement with the results obtained at 30 °C by de Wet and Haul [5] using spectrographic techniques in saturated chromium amalgams

Table 3
Solubility of chromium in mercury

T (°C)	Solubility (µg/g)	Reference
18	3.1×10^{-7}	Tammannn and Hinnüber [3]
20	<0.5	Irvin and Russel [4]
20	9.42×10^{-23}	Weeks [7][a]
Room T	0.56 ± 0.07	This work
30	0.3–0.4	de Wet and Haul [5]
500	0.18	Jangg and Palman [6]
505	0.08–0.18	Weeks [7]
530	0.23	Weeks [7]
550	0.21	Jangg and Palman [6]
550	0.26–0.34	Weeks [7]
576	0.73	Weeks [7]
600	3.11	Weeks [7]
650	7.78	Weeks [7]

[a] Value obtained using the relationship Log_{10} (ppm Cr) = 12.11–9830/T (T is temperature in Kelvin).

Table 4
Solubility of iron in mercury

T (°C)	Solubility (µg/g)	Reference
–	<13	Richard and Garrod-Thomas [34]
17	1.15×10^{-13}	Tammann and Kollmann [35]
–	0.062	Tammann and Oelsen [36]
20	0.7	Palmaer [37]
20	<0.1	Irvin and Russel [4]
20	1.07×10^{-7}	Weeks [7][a]
Room T	45.5 ± 0.4	This work
100	0.8	Palmaer [37]
211	0.7	Palmaer [37]
425	0.03	Marshal et al. [30]
500	0.56	Weeks [7]
500	0.03–0.08	Marshal et al. [30]
520	0.20	Weeks [7]
550	0.06	Weeks [7]
590	0.08	Weeks [7]
620	0.17	Weeks [7]
660	0.14	Weeks [7]
700	0.23	Marshal et al. [30]

[a] Value obtained using the relationship Log_{10} (ppm Fe) = 2.8–2700/T (T is temperature in Kelvin).

Table 5
Solubility of nickel in mercury

T (°C)	Solubility (µg/g)	Reference
–	1440	Tammann and Oelsen [36]
17	5.9	Tammann and Kollmann [35]
20	<0.2	Irvin and Russel [4]
Room T	2.6 ± 0.39	This work
30	1.3–7	de Wet and Haul [5]
400	14	Jangg and Palman [6]
450	17	Jangg and Palman [6]
500	23	Jangg and Palman [6]
500	111	Weeks [7]
550	31	Weeks [7]
550	25	Jangg and Palman [6]
590	32	Parkman and Whaley [34]
600	47	Weeks [7]
620	21	Weeks [7]
650	58	Weeks [7]
690	53–85	Weeks [7]
730	108	Weeks [7]
750	60–202	Weeks [7]

(0.3–0.4 wt ppm) and suggest that the other quoted values [3,6,33] can be discarded.

Let us continue with $x_{Fe(Hg)}^{sat}$ and the solubility values reported in Table 4. In all cases, the amount of dissolved iron found in the present work at room temperature is much higher than all experimental solubility data of the literature, given by Richard and Garrod-Thomas [34], Tammann and Kollmann [35], Tammann and Oelsen [36], or Palmaer [37], Irvin and Russel [4].

In fact, the method of filtration of Fe saturated amalgams using a chamois leather followed by distillation of mercury and colorimetric determination of metals [34], even modified by using amalgams filtration through a sintered glass [4] is not precise enough. The same comment is valid for both E.M.K. [35] and magnetic [36]

measurements. None of these methods permit to approach the solubility value we propose in the present work, based on ICP-OES measurements performed on Hg in contact with two Fe containing alloys (T91 and 316L) in variable experimental conditions and for variable durations. Thus, we propose the value, $x_{Fe(Hg)}^{sat} = 45.5 \pm 0.4$ wt ppm, as a valuable indication of the solubility limit at room temperature.

Concerning nickel, with exception of the very high solubility value found by Tammann and Oelsen [36], meaningless without indication of the temperature of the measurements, the solubility limit of $x_{Ni(Hg)}^{sat} \sim 2.6 \pm 0.39$ wt ppm obtained in this work is in very good agreement with the other literature data (Table 5).

4. Conclusions

The objective of this work was to determine the convenient surface preparation to wet by mercury the notches of center-crack tension (CCT) specimens made of T91 and 316L steels. The following results were obtained:

– Mechanical polishing is convenient to wet the notch walls of T91 CCT specimens by mercury at room temperature. 'Intimate contact' or wetting is obtained after one week according to SEM observations, whereas both Fe and Cr dissolution in Mercury is measured by ICP-OES after three weeks ageing.
– We propose the following solubility limit values for Fe and Cr in mercury at room temperature:

$$x_{Fe(Hg)}^{sat} = 45.5 \pm 0.4 \, \text{wt ppm} \quad \text{and} \quad x_{Cr(Hg)}^{sat} \sim 0.56 \pm 0.07 \, \text{wt ppm},$$

higher in both cases than the literature data.
– Other surface preparations, especially electropolishing [38], do not permit to wet T91 steel, either plates or notches, by mercury.
– Chemical etching in 4%HCl applied for 10 min allow for wetting 316L stainless steel by mercury. A good contact of mercury with the notch walls is obtained after 30 min ageing, whereas Ni dissolves quasi instantaneously into the mercury confined in the notch.
– As concerns the 316L/Hg couple, a steady state interfacial behavior is not rigorously attained after three weeks ageing, but should take some more ageing time, contrary to what happens with the T91/Hg couple, always at room temperature.
– The solubility limit of Ni in mercury attains $x_{Ni(Hg)}^{sat} \sim 2.6 \pm 0.39$ wt ppm, a value in good agreement with the literature data.
– Mechanical polishing does not permit to wet 316L, both plates and notches, by mercury, contrary to what is found with the T91/Hg couple.

The so-defined experimental procedures should be helpful to study the crack propagation using CCT specimens of 316L and T91 with notches filled with mercury.

References

[1] M.H. Kamdar, Prog. Mater. Sci. 15 (1973) 289.
[2] M. Barlow, P.J. Planting, Z. Metallkd. 10 (1969) 817.
[3] G. Tammann, J. Hinnüber, Z. Anorg. Allg. Chem. 160 (1927) 249.
[4] N.M. Irvin, A.S. Russel, J. Chem. Soc. (London) 135 (1932) 891.
[5] J.F. de Wet, R.A.W. Haul, Z. Anorg. Allg. Chem. 277 (1954) 96.
[6] G. Jangg, H. Palman, Z. Metallkd. 54 (1963) 364.
[7] J.R. Weeks, Corros. NACE (April) (1967) 98.
[8] J.R. DiStefano, S.J. Pawel, E.T. Manneschmidt, Oak Ridge National Laboratory Report, ONRL/TM-13675, September 1998.
[9] S.J. Pawel, J.R. DiStefano, J.P. Strizak, C.O. Stevens, E.T. Manneschmidt, Oak Ridge National Laboratory Report, ONRL/TM-13759, SNS/TSR-0097, March 1999.
[10] S.J. Pawel, J.R. DiStefano, E.T. Manneschmidt, Oak Ridge National Laboratory Report, ONRL/TM-13754, April 1999.
[11] S.J. Pawel, J.R. DiStefano, E.T. Manneschmidt, Oak Ridge National Laboratory Report, ONRL/TM-2000/195, July 2000.
[12] S.J. Pawel, J.R. DiStefano, E.T. Manneshmidt, Oak Ridge National Laboratory Report ORNL/TM-2001/18, February 2001.
[13] S.J. Pawel, E.T. Manneschmidt, R.P. Taleyarkhan, S.H. Kim, J.R. DiStefano, Oak Ridge National Laboratory Report, ONRL/TM-2001/086, May 2001.
[14] H. Tian, P.K. Liaw, H. Wang, D. Fielden, J.P. Strizak, L. Mansur, J.R. DiStefano, Mater. Sci. Eng. A 314 (2001) 140.
[15] S.J. Pawel, J.R. DiStefano, E.T. Manneshmidt, J. Nucl. Mater. 296 (2001) 210.
[16] J.P. Strizak, J.R. DiStefano, P.K. Liaw, H. Tian, J. Nucl. Mater. 296 (2001) 225.
[17] J.P. Strizak, L.K. Mansur, J. Nucl. Mater. 318 (2003) 151.
[18] H. Tian, P.K. Liaw, J.P. Strizak, L.K. Mansur, J. Nucl. Mater. 318 (2003) 157.
[19] K. Kikuchi, H. Kogawa, M. Futakawa, S. Ishikura, M. Kaminaga, R. Hino, J. Nucl. Mater. 318 (2003) 84.
[20] M. Futakawa, T. Naoe, C.C. Tsai, H. Kogawa, S. Ishikura, Y. Ikeda, H. Soyama, H. Date, J. Nucl. Mater. 343 (2005) 70.
[21] H. Soyama, M. Futakawa, K. Homma, J. Nucl. Mater. 343 (2005) 116.
[22] J.P. Strizak, H. Tian, P.K. Liaw, L.K. Mansur, J. Nucl. Mater. 343 (2005) 134.
[23] T.A. Gabriel, J.R. Haines, T.J. McManamy, J. Nucl. Mater. 318 (2003) 1.
[24] S. Nagamiya, J. Nucl. Mater. 343 (2005) 1.
[25] A.R.C. Westwood, M.H. Kamdar, Philos. Mag. 8 (1963) 787.
[26] G. Petzow, Metallographic Etching, ASM, 1978, 57.
[27] V. Ghetta, F. Gamaoun, J. Fouletier, M. Hénault, A. Lemoulec, J. Nucl. Mater. 296 (2001) 295.
[28] C. Guminski, J. Phase Equilib. 20 (1999) 85.
[29] S.Y. Lee, P. Nash, Binary Alloy Phase Diag. 2148 (1991).
[30] A.L. Marshall, L.F. Epstein, F.J. Norton, JACS 72 (1950) 3514.
[31] M. Venkatraman, J.P. Neumann, Bull. Alloy Phase Diag. 10 (1989) 157.
[32] L.F. Kozin, Fiziko-Khimich, Osnovy Amalgamnoi Metallurgii, Nauka, Alma-Ata, 1964.
[33] Z. Galus, C. Guminski, in: C. Hirayama (Ed.), Metals in Mercury, vol. 25, Pergamon, 1986.
[34] T.N. Richard, R.N. Garrod-Thomas, Z. Phys. Chem. 72 (1910) 165.

[35] G. Tammann, K. Kollmann, Z. Anorg. Allg. Chem. 160 (1927) 242.

[36] G. Tammann, W. Oelsen, Z. Anorg. Allg. Chem. 186 (1930) 257.

[37] Palmaer, Z. Elektrochem. Angew. Phys. Chem. 38 (1932) 70.

[38] D. Gorse, in: Handbook on Lead-bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal-hydraulics and Technologies, OECD/NEA, 2007, p. 275 (Chapter 7).