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ScienceDirect
Journal of Nuclear Materials 376 (2008) 330–335
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Heat treatment effect of T91 martensitic steel on liquid metal embrittlement

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Abstract

The sensitivity of liquid metal embrittlement of the T91 martensitic steel is investigated with small punch tests at 300 °C in air and in lead bismuth eutectic (LBE). The material was studied in six tempering conditions corresponding to different values of hardness. An effect of LBE has been observed for all the materials excepted for T91 steel tempered at 750 °C, the more ductile material. In high strength materials (T91 steel as quenched, tempered at 600 °C or 500 °C), a ductile to brittle transition is induced by liquid metal, confirmed by the observation of brittle fracture. In relative high strength materials (tempered at 650 °C and 700 °C), LBE promotes a decrease in mechanical properties and a reduction of the ductility of materials, with a mixed ductile and brittle fracture.

1. Introduction

In order to be compatible with liquid metals, structural materials must satisfy several requirements essentially related to corrosion resistance and liquid metal embrittlement (LME) prevention. For the latter case, it has been demonstrated that the concept of specificity based on the apparent immunity of some liquid metal–solid metal couples is not relevant [1–3], and therefore the question has to be reformulated. Especially, for the reliability of materials for heavy liquid metal (HLM) Cooled Reactors and Related Technologies, it is better to find out the specific conditions for the occurrence of LME. For the T91 steel which is a material of prime interest for HLM nuclear systems such as accelerator driven systems (ADS) and Generation IV nuclear concepts, the importance of the heat treatment on LME was observed [3–5]. LME of the T91 martensitic steel in lead bismuth eutectic (LBE) was observed with specific monotonic tensile test experiments [3,4] and with small punch tests [5]. A special heat treatment leading to a high hardness value was applied on the material to observe this effect. The comparison of the results of the conventional tensile tests and the small punch tests (SPT) showed that SPT is more sensitive in the evidence of LME [5]. In SPT, specimens shaped as disk are punched in their middle by a ball. This test, here adapted in presence of a liquid metal, is attractive for the characterization of material the quantity of which is scarcely available or need to be reduced (e.g. irradiated materials, determination of residual life of components in service ...).

The objective of the present paper is to study liquid metal embrittlement sensitivity of the T91 martensitic steel according to different heat treatments by small punch tests at 300 °C in air and in liquid LBE.

2. Material and experimental procedure

2.1. Material and the heat treatments

The T91 martensitic steel used in this investigation, supplied by Ascometal has the chemical composition given in Table 1. The standard heat treatment consists of an austenisation at 1050 °C for 1 h followed by air cooling and subsequent tempering for 1 h at 750 °C. The microstructure

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doi:10.1016/j.jnucmat.2008.02.018

consists of a tempered martensite with an average prior austenite grain size of about 20 μm.

Six different heat treatments were studied: the standard heat treatment (noted as 'TR750') as described above, a normalized heat treatment at 1050 °C followed by air cooling without tempering (noted as 'T'), a normalized heat treatment at 1050 °C followed by air cooling and subsequent tempering for 1 h at 500 °C (noted 'TR500'), at 600 °C (noted 'TR600'), at 650 °C (noted 'TR650'), at 700 °C (noted 'TR700'). The heat treatments only differ in their tempering temperatures which do not affect the grain size (about 20 μm) but modify the precipitation state and the recovered structures of dislocations. This leads to different macro hardness HV_{10} values (see Table 2).

2.2. Small punch test setup

A specific setup was used to perform SPT in air and in liquid metal (Fig. 1). It consists of a disk specimen holder, a pushing rod and a ball. The specimen holder includes a lower die and an upper die which is also used as the tank for the liquid metal. The load is transferred onto the specimen by means of a pushing rod and a 2.5 mm diameter tungsten carbide ball in contact with the lower surface of the disk specimen. In this way, the puncher being under the specimen, the upper surface of the specimen is in contact with the liquid metal and is submitted to tensile loading. T91 rods were machined into cylindrical bars 8.9 mm in diameter and gently sliced with a controlled load saw to disk 600 μm in thickness. Before testing, the sample surfaces were mechanically polished with SiC paper up to 1200 grade and then electro polished, in order to avoid effects due to the roughness of the surface and residual stresses developed during the mechanical polishing. The final thickness was 500 (±25) μm. SPT were performed using an electro mechanical machine with a controlled cross-head speed of 0.5 mm/min. Load–cross-head displacement curves were recorded during the tests. The tests were carried at 300 °C, in laboratory air or in LBE (56 at.%Bi–44 at.%Pb) without any particular care to control or measure the oxygen activity. A heat ring surrounded the setup with the specimen and the liquid metal. The temperature was controlled by a thermocouple placed 3 mm away from the specimen and the test was started 10 min after the setting temperature was reached. At least five tests per each test condition have been performed.

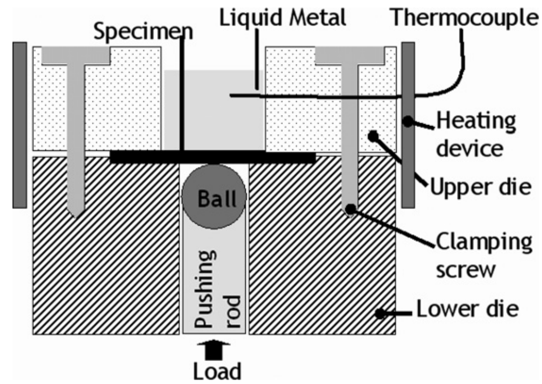

Fig. 1. Small punch test setup.

Table 1
Chemical composition of the T91 steel (wt%)

Element	Cr	Mo	V	Mn	Si	Ni	C	Nb	Fe
	8.50	0.95	0.21	0.47	0.22	0.12	0.10	0.06	Bal

Table 2
Hardness (HV_{10}) of T91 steel according to the heat treatment

Heat treatment	T	TR500	TR600	TR650	TR700	TR750
HV_{10}	380 ± 5	396 ± 5	374 ± 3	318 ± 3	285 ± 1	256 ± 5

After fracture in LBE, dissolution of the remaining liquid metal on the fracture surfaces was achieved with a solution of acetic acid, hydrogen peroxide and ethanol. This allowed fractographic investigations performed on a FEI Quanta 400 scanning electron microscope (SEM) using secondary and backscattered electrons to identify the fracture modes.

3. Results

3.1. SPT in LBE

The load–displacement curves obtained at 300 °C in air for the T91 steel according to the six heat treatments are shown in Fig. 2(a). The curves for TR600, TR650, TR700 and TR750 materials exhibit the typical feature of a ductile behavior [6–8] with the presence of four stages. The first stage, noted as '❶' on the curve in Fig. 2(a), corresponds to the elastic bending. While the entire sample undergoes an elastic deformation, the ball-sample contact area, which is very small in size, is plastically deformed. The second stage (noted as '❷') corresponds to a plastic bending state: the volume of the sample which is plastically deformed progressively increases spreading from the ball-sample contact area through the overall thickness and in radial direction. Then a stretching of the membrane occurs in the third stage (noted as '❸'). At this stage, the deformation of the sample is not caused by bending but by stretching around the contact area between the ball and the sample. Microcracks are generated during this stage. Finally, during the fourth stage where the load reaches its highest value (noted as '❹'), the main crack forms and propagates. In fact, there is no clear boundary between the different stages from a physical point of view: one stress state is predominant compared to another one. Moreover, the displacement–load curves for the TR500 and T materials appear to be not conventional for ductile behavior but were however reported by other authors [6].

The studied materials differ by some typical values measured from the curves such as the maximum load F_m, the

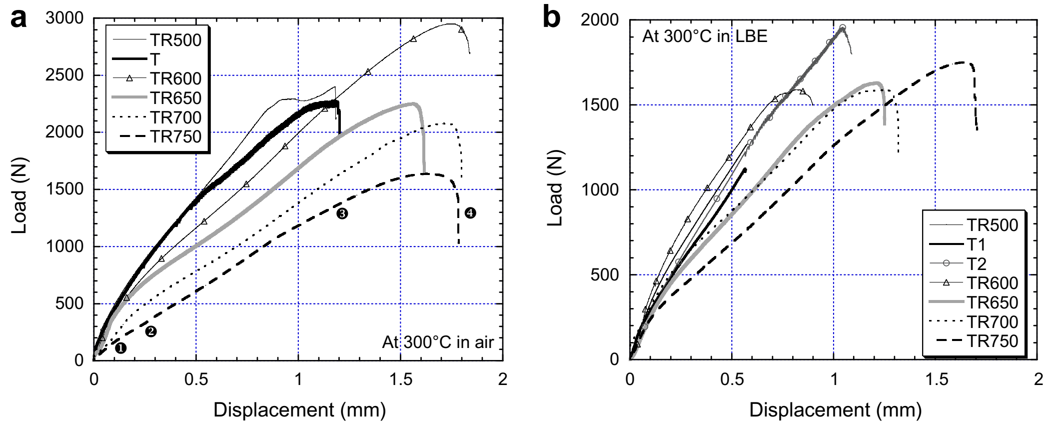

Fig. 2. Load–displacement SPT curves of the T91 steel according to the heat treatment and tested (a) in air at 300 °C and (b) in LBE at 300 °C.

fracture energy (derived from the area under the load versus displacement curve) J_f and the displacement to fracture d_f. The results for the different materials are given in Table 3 (the results are the mean values of several small punch tests). In agreement with the hardness and due to the tempering at 750 °C, the standard heat treatment T91 has the smaller maximum load (Table 3). The TR650 and TR700 materials with intermediate values of hardness between the TR600 and TR750 materials have also intermediate values of F_m. The distinguishable responses of the T and TR500 materials, associated with strongly reduced mechanical values (F_m, d_f) in comparison with the TR600 material are probably due to cracking and particularly to the propagation of the cracks formed during the third stage (the membrane stretching).

For the TR600, TR650, TR700 and TR750 materials, cracking is circular and the fracture surface is ductile (Fig. 3(c)–(g)). These results are in agreement with a cracking mechanism due to membrane stretching and with the observations mentioned for a ductile fracture behavior [6–9]. For the T and TR500 materials, the circular crack is accompanied with radial ones (Fig. 3(a) and (b)). The radial cracks are more numerous and shorter in the TR500 material than in the T one. The fracture surface is ductile as observed after tests in air for the TR600, TR650, TR700 and TR750 materials.

3.2. SPT in LBE

Fig. 2(b) and Table 4 give respectively the load displacement curves and the typical values measured from the curves of the tests performed at 300 °C in LBE.

The tests carried out on the TR750 material at 300 °C in LBE provided a response similar to that in air. The load–displacement curves recorded during the tests performed in LBE have the same shape and the same typical values as those recorded during tests in air. In LBE as in air, at 300 °C, the cracking is circular (Fig. 4(g)) and the fracture is ductile.

The behavior of the other materials in LBE contrasts with that observed in air.

The load–displacement curve of the TR500 material is quasi linear up to failure, exhibits a very little plastic bending and zero plastic membrane stretching. This curve is typical of a brittle behavior [7,8,10] generally resulting from irradiation or low temperature effect, but here in the present case from the presence of LBE at 300 °C. The tests performed on the T material in LBE at 300 °C give rise to two kinds of curve. The first kind of curve, noted as ‘T1’, has all the features (quasi linear response, weak maximum force), suggesting a brittle behavior as for the TR500 material. The second one noted as ‘T2’, not linear right to failure and with a rather large maximum load, does not exhibit the character for a brittle behavior nor a clear ductile one. The curve of the TR600 material is similar to the curve of material noted T2. The general tendency for the T, TR500 and TR600 materials fractured at 300 °C in LBE is that cracking initially appears semi-circular and then tends to propagate outwards in a radial direction (Fig. 4(b)–(d)). In some samples, radial cracks without semi-circular cracking (Fig. 4(a)) are observed as for brittle behavior [6–9]. All the fracture surfaces of the T, TR500, TR600 materials tested in LBE are always brit-

Table 3
Average values of key points measured in the small punch tests at 300 °C in air

Heat treatment	T	TR500	TR600	TR650	TR700	TR750
F_m (N)	2311 ± 150	2185 ± 150	2942 ± 65	2216 ± 32	2071 ± 56	1655 ± 45
J_f (J)	1.79 ± 0.17	1.67 ± 0.20	3.30 ± 0.15	2.28 ± 0.06	2.17 ± 0.18	1.66 ± 0.10
d_f (mm)	1.22 ± 0.07	1.18 ± 0.10	1.83 ± 0.05	1.70 ± 0.08	1.72 ± 0.07	1.67 ± 0.09
Fracture surface	Ductile	Ductile	Ductile	Ductile	Ductile	Ductile

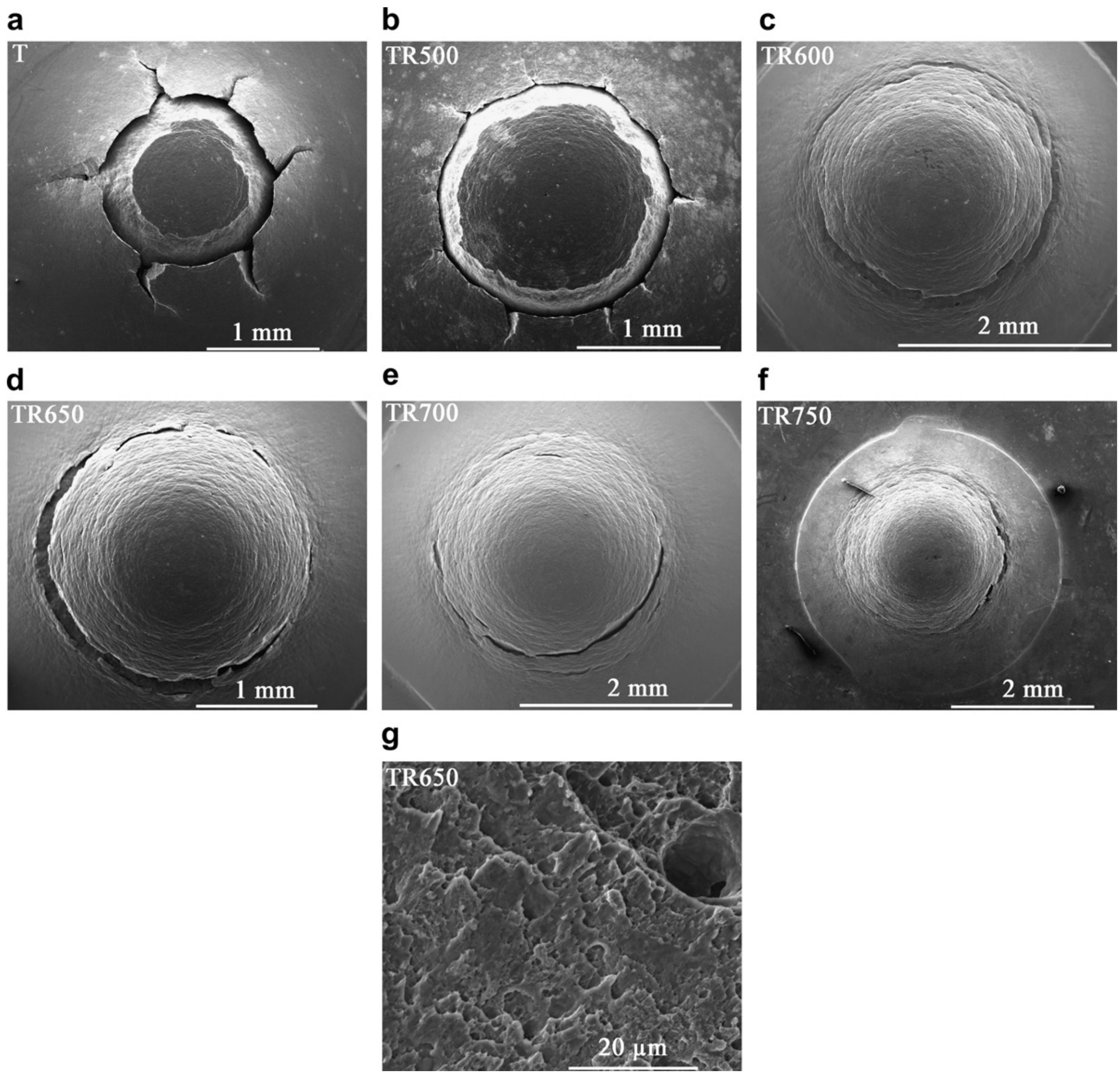

Fig. 3. SEM micrographs showing cracked surfaces and ductile fracture surface of samples tested in air at 300 °C.

Table 4
Average values of key points measured in the small punch tests at 300 °C in LBE

Heat treatment	T1	T2	TR500	TR600	TR650	TR700	TR750
F_m (N)	1105 ± 150	2014 ± 100	1295 ± 200	1524 ± 160	1656 ± 44	1705 ± 200	1762 ± 100
J_f (J)	0.33 ± 0.07	1.27 ± 0.25	0.39 ± 0.09	0.96 ± 0.15	1.35 ± 0.08	1.44 ± 0.22	1.8 ± 0.15
d_f (mm)	0.5 ± 0.06	1.04 ± 0.10	0.54 ± 0.08	0.94 ± 0.10	1.28 ± 0.05	1.37 ± 0.12	1.66 ± 0.11
Fracture surface	Brittle	Brittle	Brittle	Brittle	Mixed	Mixed	Ductile

tle, essentially transgranular (Fig. 5(b)) with some occasional intergranular decohesion (Fig. 5(a)). The decrease in the typical values F_m, J_f and d_f in theses three cases (T, TR500 and TR600) for tests performed in LBE in comparison with tests in air is in agreement with the observed brittle fracture in LBE.

As in air, the curves for the TR650 and TR700 materials tested in LBE exhibit the typical feature of a ductile behavior. But the typical values F_m, J_f and d_f are smaller for tests performed in LBE in comparison with tests in air. The decrease is more important in the case of the TR650 material.

Unlike tests in air, the circular crack is accompanied with small radial ones (Fig. 4(e)). The latter are very short in the TR700 material and sometimes absent (Fig. 4(f)). The TR650 and TR700 materials fractured in LBE at 300 °C exhibit fracture surface essentially ductile, but with some brittle zones (Fig. 5(c) and (d)), located as well in the center as near the external part exposed to the LBE. In the radial cracks, the brittle zones appear more important.

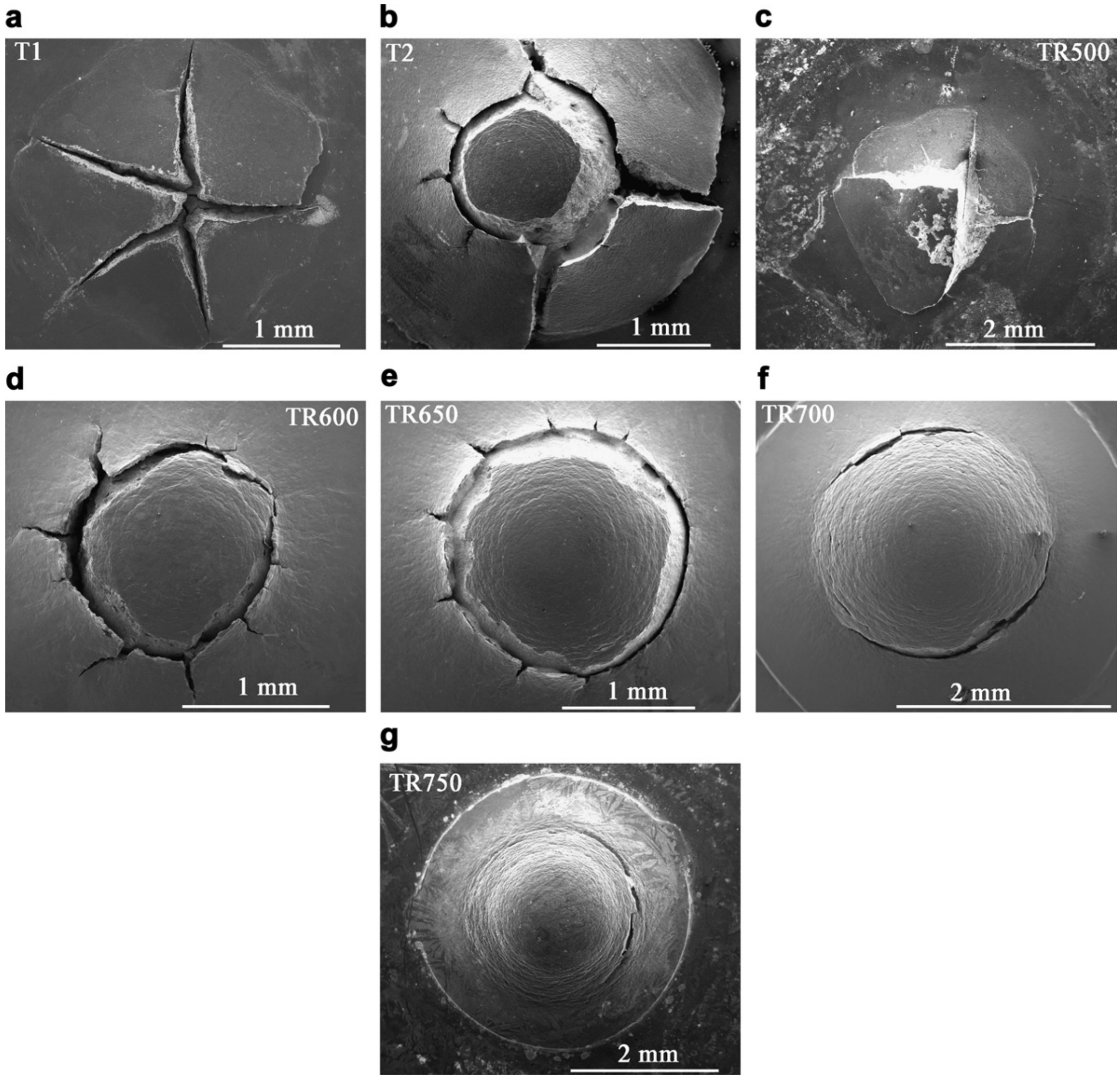

Fig. 4. SEM micrographs showing cracked surfaces of samples tested in LBE at 300 °C.

4. Discussion

In general the T91 steel is a ductile material at 300 °C in air and in LBE [3,4,11]. But a hard microstructure combined with a sharp crack nucleation in a liquid metal plays an important role on the occurrence of LME. It has been proposed that the main reason for LME is a decrease of local fracture toughness K_{IC} caused by adsorbed atoms which involves real wetting of the steel by the liquid metal [3,4,11,12].

According to the hardness value related to a specific heat treatment, differences in SPT responses in LBE at 300 °C were observed for the T91 steel. A ductile to brittle type response transition induced by liquid metal has been observed for the high strength materials (T, TR500 and TR600). This transition is associated with ductile fracture in air and brittle facture in LBE, and with a decrease in the displacement at fracture, of the maximal load and of the fracture energy. In the case of the SPT, the fatal crack seems to initiate at the surface of the specimen [13]. Indeed, during punching, the material is submitted to shear deformation with matter displacement higher in the external part exposed to the liquid metal than the inner part. This can promote transgranular slip, large offsets of matter and a plasticity induced roughness with large fresh metal areas on which liquid metal atoms can adsorb and trigger further brittle fracture. This could explain why a fully brittle fracture is observed on the TR500 material when it is punched in the liquid metal. To fill with liquid metal a ductile crack that nucleated in the bulk but near the surface with liquid metal is not likely. Indeed, in this case, the fracture surface should comprise a ductile fracture located near the external part associated with a brittle part located more in depth. In addition, crack nucleation near the surface involving the evolution of micro voids seems to be not very promoted as indicated by the behavior of the T or TR600 materials. The TR600 material and in some cases the T material exhibit large value of stress but fully brittle surface.

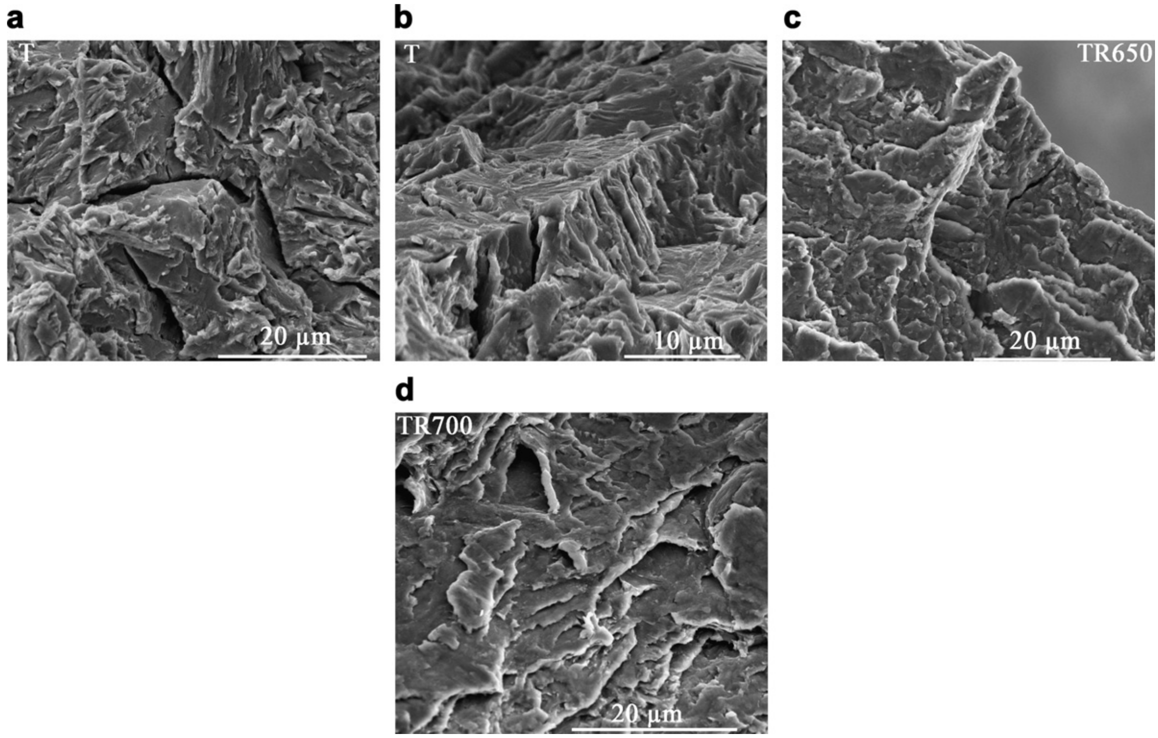

Fig. 5. SEM fracture surface after tests in LBE at 300 °C showing intergranular brittle fracture occasionally observed (a), transgranular brittle fracture mostly observed (b) and mixed fracture near the external part exposed to the LBE (c), in the middle of the fracture surface (d).

In the case of more ductile materials, as TR650, TR700 and TR750, the propagation of the main brittle fracture is not possible because of the ductility of materials and so of their large plastic deformation. The local brittle fracture due to LBE can be explained by the formation of very sharp defects in liquid metal during the propagation of ductile cracks or on the surface of samples in contact with LBE. This induces good wetting and stress concentration for a relative high strength material (TR650 and TR700 materials), which are necessary conditions to promote brittle fracture. The propagation of brittle cracks is probably limited by the blunting of the crack tip due to the plastic deformation of the material. The local brittle fractures observed for the TR650 and TR700 materials induce the decrease in the values F_m, J_f and d_f.

5. Conclusion

In the present work, the sensitivity to liquid metal embrittlement of the T91 steel as function of the heat treatment was studied by SPT carried out at 300 °C, in air and in LBE. In air, the tempering heat treatments performed on the T91 steel affected the mechanical properties of the materials, while the steel remained ductile regardless of the tempering condition. However, for tests in LBE, a brittle fracture associated with a peculiar mechanical response was observed for the non tempered T91 steel or tempered at 500 °C and at 600 °C, i.e. the hardest materials. On intermediate high strength material, T91 tempered at 650 °C or tempered at 700 °C, LBE promotes a ductile behavior but with mixed ductile and brittle fracture and a reduction of mechanical properties measured by SPT (F_m, J_f and d_f).

Acknowledgements

This work has been supported by the French CNRS GdR GEDEPEON and by European projects of the 5th and 6th FP EURATOM program. Ascométal Dunkerque is acknowledged for providing the material.

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