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Effect of contact conditions on embrittlement of T91 steel by lead–bismuth

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Abstract

The T91 martensitic steel is a candidate structural material for the liquid lead–bismuth eutectic (LBE) MEGAPIE spallation target. This paper first reviews some results on Liquid Metal Embrittlement (LME) of martensitic steels by liquid metals. It appears that LME of steels can occur provided a few criteria are fulfilled simultaneously. Intimate contact between liquid metal and solid metal is the first one. Usually, it is impossible to avoid the oxide film formation on the steel surface even after short exposure to air. This explains the difficulty arising when one would like to determine the susceptibility to LME of T91 steel whilst put into contact with lead–bismuth. Later, we report on different methods of surface preparation in order to remove the oxide layer on the T91 steel (PVD, soft soldering fluxes) and the resulting susceptibility to LME.

1. Introduction

It is useful here to recall the definition of LME given by Kamdar [1]: LME may be considered as a special case of brittle fracture. The effects of mechanical, metallurgical, physical and chemical factors on embrittlement may be explained rationally in terms of the principles of brittle fracture.

In specific conditions, high strength martensitic steels are reported to be embrittled by many low melting point liquid metals (Pb, Sn, Hg, Bi, Cd) [2]. Some of the results point out the metallurgical state, in particular the role of hardening heat treatment which increases the susceptibility to LME. Some examples are given therein together with new results on a 9Cr steel (T91) in contact with Pb–Bi alloy.

Balandin and Divisenko [3] reported on the mechanical behaviour of the 12KhM Russian steel (0.12C–1Cr–1Mo) in contact with lead–bismuth eutectic. Their main results are the following:

- surface state preparation affects the mechanical properties, severe embrittlement being observed as a result of pre-wetting using chemical fluxes;
- strain rate has a strong influence on the embrittling effect;
- the effect is maximum around the temperature of 400 °C.

The interpretation is based on the Rebinder effect: a decrease of the surface energy due to contact with surface-active media. The previously mentioned authors attributed the ductility recovery above 400 °C to a 'protection effect' by oxidation starting at the onset

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temperature for fast oxidation kinetics (of the order of 400 °C).

Popovitch and Dmukhovskaya [4,5] link the embrittling effect to the Dynamic Strain Ageing (DSA) phenomenon exhibited by the studied steels in the same temperature range. Their interpretation of LME [6,7] is that the occurrence of bulk hardening by DSA, jointly with a decrease in the surface energy, leads to an increased surface plasticity. This explains the development of cracks from the surface and brittle fracture. The recovery temperature then simply indicates the end of the DSA range.

In another context, Warke, Breyer and co-workers [8–10] found a severe loss of ductility on leaded steels (AISI 4145: 0.4C–0.9Mn–1Cr–0.3Si–0.3Pb) in the temperature range between 200 and 400–450 °C. They also demonstrated that 'the elevated temperature embrittlement of leaded steels could be duplicated in experiments where lead and lead alloys were soldered to the surface of non-leaded tensile bars'. They therefore claimed that the high temperature embrittlement of leaded steels is a manifestation of LME. The temperature of ductility recovery is found to be dependent on the chemical composition of lead alloys.

Gordon and An [11,12] modelled Metal Induced Embrittlement (MIE), taking into account data available on Solid-Metal Embrittlement on delayed rupture. In the proposed mechanism, below the melting point, the embrittling atoms penetrate by stress-aided (and possibly by dislocations aided) diffusion at short distance into the base metal grains boundaries where crack nucleation can take place. Above the melting point, the transport time of the embrittling atoms is too short so that the crack initiation process becomes rate-controlling throughout.

In all previously mentioned studies, reference is made to a chemical cleaning of the surface. The method used is to remove the oxide layer using a soft soldering flux composed of zinc chloride added to ammonium chloride. This flux is known to promote wetting of low melting point soldering alloys on steel [13,14]. Some checks against chloride cracking and zinc effect are also reported in the previous references: the effect of these contaminations was not considered important.

In his review paper of 1970, Kamdar [1] stipulates that the phenomenology will concern oxide-free solid metals coated with a film of liquid metal. Concerning the 'T91/PbBi' couple, it is needed at the same time:

- To produce oxide-free T91 steel specimens to evaluate the intrinsic embrittling character of the 'T91/Pb–Bi' couple;
- To determine the changes in the LME susceptibility as a function of the properties of the interfacial oxide on T91 when varying the environmental conditions.

The second point is especially important for in-service steel protection. A stable oxide growth is not only important for corrosion protection but also for preventing direct contact with the liquid metal, thereby excluding LME concerns. The evolution of the intimate contact with time due to corrosion processes must be carefully investigated.

In this paper, the problem of intimate contact is dealt with by use of physical vapour deposition technique (Section 2.1) or chemical fluxing (Section 2.2). The results are compared with the ones obtained without specific wetting treatment (Section 2.3).

2. Experiments on T91 steel in contact with Pb–Bi alloy

T91 steel is kept in its standard metallurgical state. All specimens are tested in the as received state: austenitisation at 1050 °C for 1 h, air quenching followed by tempering at 750 °C for 1 h. The chemical composition of T91 steel is given in Table 1.

2.1. Direct contact via physical vapour deposition [15]

Smooth cylindrical tensile specimens are used. Particular attention is paid to the surface preparation in order to remove the native oxide. The specimens are cleaned by ion beam sputtering in an UHV chamber, followed by physical vapor deposition of lead bismuth (60Pb–40Bi). The coating thickness is of the order of few hundreds of nanometers. The surface composition is monitored by using auger electron spectroscopy (AES). Being protected from re-oxidation by deposition of a Pb–Bi alloy, the specimens can be transferred in air, at room temperature, into the tensile test cell. The tensile tests are carried out at 340 °C under flowing helium

Table 1
Chemical composition of the T91 steel plates (wt%, balance Fe) supplied by Creusot Loire Industrie

C	Mn	P	S	Si	Cr	Mo	Ni
0.105	0.38	0.009	0.003	0.43	8.26	0.95	0.13
V	Nb	N	Al	Cu	As	Sn	Ti
0.2	0.08	0.055	0.024	0.08	0.02	0.008	0.014

[15]. Clear LME effects are evidenced using this surface preparation of the T91 test bar.

A mixed brittle/ductile rupture is observed. Brittle fracture occurs only at the periphery of the fracture surface. Brittle crack propagation is controlled by liquid metal supply at the crack tip due to the limited amount of Pb–Bi deposited (the coating thickness being of the order of few hundreds of nanometers). Our explanation for the mixed fracture mode is the following: cracks are initiated at the surface during plastic deformation. Some liquid metal flows into cracks by capillarity. As the crack propagates, some liquid metal remains on the crack surface thereby progressively emptying the reservoir. Ductile behaviour is recovered once no more liquid metal can be supplied at the crack tip. Therefore, the mechanical degradation displayed with the tensile curve (Fig. 1) would be more important in the presence of a larger reservoir of liquid metal. The rupture occurs mostly by quasi-cleavage in areas wetted by Pb–Bi as can be seen from Fig. 1(c).

2.2. Intimate contact by means of chemical fluxes

Contact can also be obtained by means of soft soldering fluxes (mixture of zinc chloride with 7 wt% of ammonium chloride). The idea is to dissolve the oxide film in the flux and to coat the specimen with liquid Pb–Bi protected from air by the flux to prevent re-oxidation. Smooth specimens were prepared by soldering Pb–Bi on the surface. Quasi-cleavage cracking is also observed using this surface preparation technique.

The crack propagation is also limited by supply of liquid metal at the crack tip as can be seen from Fig. 2(a) and (b). Ductile recovery is observed leading to crack tip blunting when liquid metal is no longer provided at the crack tip. The crack branching seems to be very little influenced by the prior austenitic microstructure as can be evidenced from Fig. 2(c) In these tests, intimate contact is only partially reached on the overall specimen surface. Areas in direct contact are sufficient to induce brittle cracking. The impurities

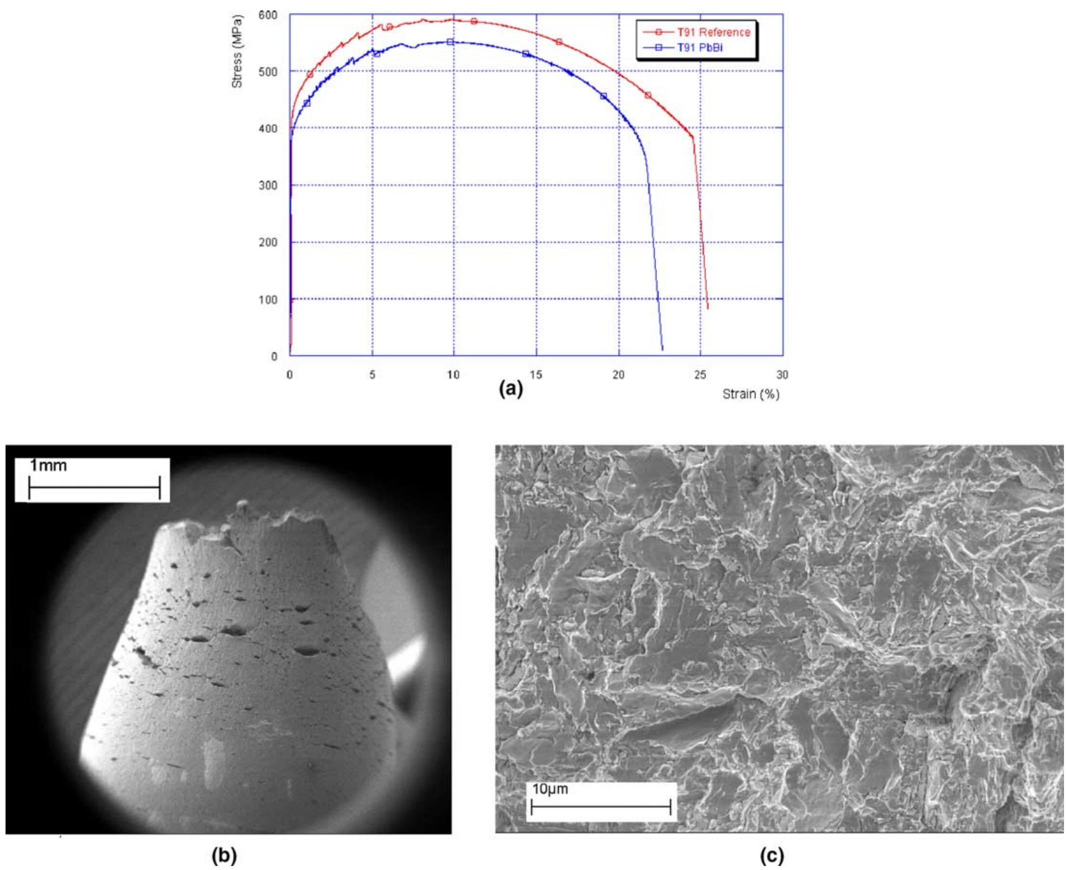

Fig. 1. In case of direct 'T91-LBE' contact obtained by ion beam sputtering in a UHV chamber prior to deposition of lead–bismuth, LME effects are produced: (a) decrease in strength and elongation to rupture as a result of tensile testing under helium; (b) multi-cracking of the gauge length of the specimen, as a result of transgranular failure initiated from the surface and (c) top view of a transgranular rupture facies of a crack initiated at the surface.

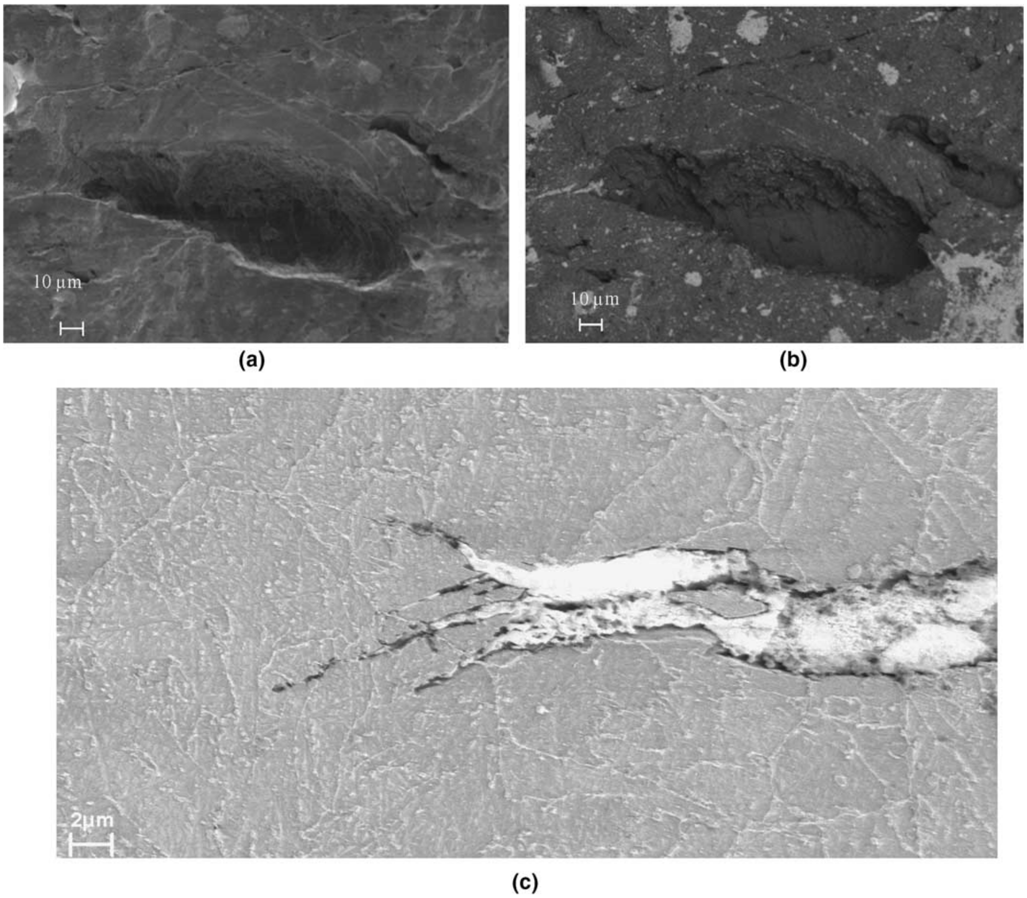

Fig. 2. In case of intimate 'T91-LBE' contact obtained by using a soldering flux to treat LBE, LME effects are produced at 350 °C: (a) and (b) brittle crack initiating from the surface and crack tip blunting when the liquid metal supply is exhausted (SE2 and BSE views) (c) cross-section of the specimen after tensile testing showing a crack filled with Pb–Bi. The microstructure is revealed with the Villela reactive.

introduction at the interface may modify the severity of embrittlement in an uncontrolled manner and constitutes the main drawback of the method. Indeed, one finds traces of fluxes by EDX analysis on the surface of the specimen, coming most likely from residual flux due to the soldering process. Nevertheless, no contamination is detected along the cracks.

2.3. Indirect contact via an oxide film [16]

In this case, the T91 test bar is simply aged in stagnant lead–bismuth for 12 h at 350 °C with a He–4%H_2 cover gas. This is sufficient to produce a porous interfacial oxide as seen below in Fig. 3. Hydrogen gas was mixed to helium to improve the 'T91-LBE' contact conditions.

The importance of the ductility reduction was found to depend on the deformation rate against oxidation rate. The maximum reduction in strength and elongation to rupture is seen in the case of a T91 corroded by contact with LBE under hydrogenated helium, using the appropriate deformation rate for the testing temperature of 350 °C. However in these experimental conditions, T91 was not aged enough in contact with LBE to attack sufficiently the oxide layer and to insure the intimate 'T91-LBE' contact ideally required to observe brittle failure. It is very likely that long exposure to strongly reducing conditions can promote oxide dissolution and intimate contact of the liquid metal with the steel.

3. Concluding remarks

We recalled that, in specific conditions, martensitic steels are found to be susceptible to embrittlement by many low melting point liquid metals. The results presented in this paper with T91 in its standard metallurgi-

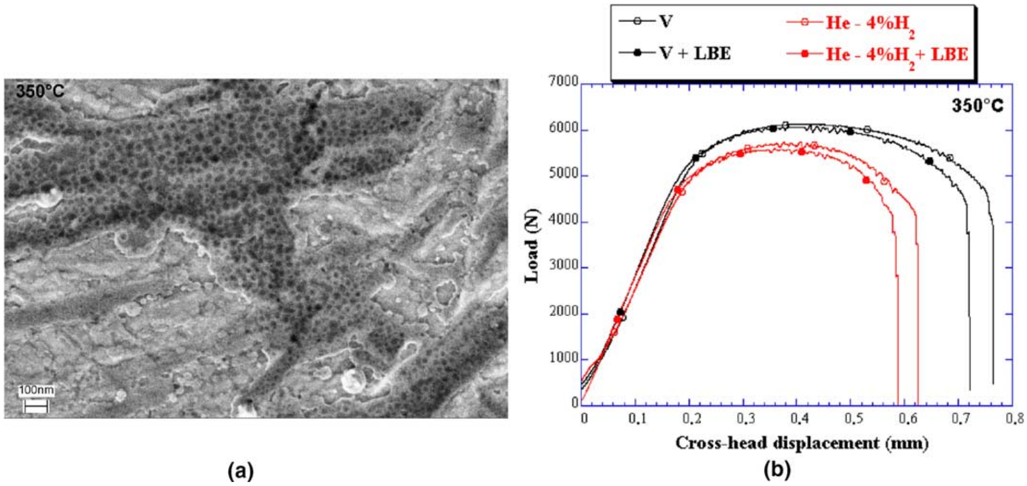

Fig. 3. (a) SEM micrograph showing the growth of a porous oxide has grown on T91 steel after 12 h exposure to lead–bismuth at 350 °C; (b) corresponding tensile curves obtained on notched specimens, whose surface state is the one presented on the left.

cal state show that embrittlement by Pb–Bi is dependent on the intimate contact requirement. Going from indirect contact, through an oxide layer, to intimate contact obtained by physical or chemical means, i.e. PVD or chemical flux, a clear change in the rupture mode from ductile to brittle for T91 steel has been displayed. The rupture mode is of quasi-cleavage type with little influence of the prior austenitic microstructure. One consequence of this work is that LME studies should comply with the intimate contact requirements. Otherwise, one should take into account the natural oxide barrier in the interpretation, especially when dealing with chromium containing steels.

Speculatively, the occurrence of brittle failure allows the use of a simple analysis to qualitatively estimate irradiation effects on LME in a typical spallation spectrum. The brittle cracking process can possibly be analyzed by the classical Cotrell–Petch view of competition between elastic fracture and plastic deformation [17]. If the maximum tensile stress is controlled by the surface energy, adsorption of a liquid metal will lower the maximum stress before cleavage. After exposure to a fast neutron spectrum or to proton irradiation, the yield strength is increased especially at low working temperature (<400 °C) [18]. In the irradiation hardening temperature range, it is not unthinkable that it should lead to an increased susceptibility to LME in case of direct contact with the liquid metal.

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