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# Liquid metal embrittlement susceptibility of T91 steel by Lead-Bismuth

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Keywords : Liquid metal embrittlement, martensitic steels, Auger electron spectroscopy (AES), physical vapour deposition (PVD), mechanical properties

## Abstract:

Previous studies on T91 steel in its standard metallurgical state found no evidence for Liquid Metal Embrittlement (LME) by eutectic Pb-Bi. In this paper, we report clear evidence that this steel can be embrittled by Pb-Bi when direct contact between the steel and the liquid metal is obtained by prior ion beam sputtering.

## Introduction:

Study of LME of steels by Pb-Bi is of renewed interest in the context of structural materials for Accelerator Driven System (ADS). These systems aim at burning nuclear waste in a sub-critical core with a powerful neutron source to maintain a stationary neutron flux. The liquid eutectic Pb-Bi serves as cooling fluid, as well as the neutron production media by spallation reactions with high energy protons. The structural components will therefore be exposed to Pb-Bi and will be subject to corrosion, irradiation and LME. The martensitic T91 steel, a modified 91 grade steel, has been selected as one of the candidate material for ADS and spallation targets because of its good mechanical strength and irradiation resistance in a fast neutron or a spallation spectrum [1].

Previous studies on LME for 91 grade steels with Pb or Pb-Bi concluded that the steel is not sensitive in its standard metallurgical state but becomes notch sensitive only after a hardening heat treatment consisting of a low temperature tempering treatment [2, 3]. In the hardened state, the rupture mode was interpreted with the model of reduction of surface energy induced by the liquid metal adsorption [4]. The engineering implication is that heat affected zones of welds are critical if no post-weld heat treatment is performed. A similar conclusion was reached in studies of F82H steel with Pb-17Li [5]. This finding led the authors to the conclusion that no pre-treatment to enforce intimate contact was needed since LME can be observed in the hardened state. Therefore, the absence of LME on standard T91 steel in these conditions was thought to mean that, in such metallurgical state, the steel is not subject to LME. Other studies focused on interaction between corrosion under reducing conditions and manifestation of LME on mechanical properties [6]. Samples were exposed to hydrogenated cover gas prior and during tensile testing in order to promote direct contact between the steel and liquid metal. In this latter work, no brittle crack propagation was observed on standard T91 but only a reduction in energy to rupture. Overall, these results show the difficulty in mechanical testing with liquid Pb-Bi to obtain direct contact as required by the phenomenological rules for LME with this type of passivable steel.

This paper reports work to clarify the issue of whether or not special metallurgical conditions or stress tri-axiality (notch effect) are needed to observe LME. It is also a demonstration that for mechanical properties in liquid metal, intimate contact is an absolute pre-requisite because the passive layer can be very effective to protect the steel against LME.

There are several means to force direct contact. The one most common method cited in the literature is, via a chemical means using soft soldering fluxes such as a mixture of zinc chloride with additions of chloride ammonium or hydrochloric aniline [7, 8]. These fluxes however lead to contamination problems with zinc, which is a known steel embrittler. They can also lead to suspicion of chloride cracking. Here, we report on the use of physical techniques deposition under vacuum, since this ensures that the problems previously encountered can be avoided. We used PVD technologies as it seems more adequate to avoid contaminants and ensure reproducibility.

## Experimental

### Materials

Cylindrical tensile specimens (4 mm diameter and 15 mm gauge length) were machined from standard T91 steel from CLI (Creusot Loire Industrie). The steel composition, analysed by the supplier, is given in table I. The specimens were used in the as-received state: austenitisation at 1050°C and tempering at 750°C. The Vickers hardness is of the order of 220 Hv. The microstructure is fully martensitic with prior austenite grains of 20 µm mean size. The eutectic Pb-Bi used in this study was provided by MetalEurop and was a 99.99% purity grade. The impurity level of Pb-Bi was analysed by ICP on one small sample and is given in table II.

### Sample preparation

Mechanical testing samples were diamond polished down to 1 µm and washed in acetone using ultrasonic treatment. Afterwards, they were introduced into a Ultra High Vacuum (UHV) surface analysis system ( $2 \cdot 10^{-10}$  mbar) where an ion etching cleaning process was applied until the natural oxide layer was completely removed. The surface composition was monitored by Auger Electron Spectroscopy (AES) in the derivative acquisition mode (energy resolution) with a cylindrical mirror analyser (CAMECA OPC 105) equipped with a coaxial electron gun operating at 2.5KV primary electron energy and 30° incidence with the sample surface normal. Ion etching is obtained using krypton ions ( $5 \cdot 10^{-8}$  mbar Kr in the analysis chamber) of 3 KeV with a differentially pumped Riber CI-50 RB ion gun.

Before sputtering (Figure 1-a), the sample is covered with a mixture of external iron oxides (and hydroxides) and inner chromium oxides as revealed by depth profiling, very similar to passive layers formed on iron-chromium alloys [9]. Some carbon and chlorine traces are also depicted: they usually remain from the post-polishing sample cleaning procedure. After their elimination by ion etching, only a small residual oxygen contaminant level remains at about 10% monolayer (Figure 1-b). All the surface gauge length can be sputtered using a rotating sample holder. Clean specimen is transferred into an auxiliary chamber ( $10^{-8}$  mbar) to undergo the metal deposition treatment. A Pb-Bi piece heated in a Ta boat by Joule effect constitutes the source for the metal evaporation towards the gauge closely located onto the transfer rod. According to Honig [10], the vapour pressures of Pb and Bi are

similar; nevertheless their evaporation rates should lead to a lead enrichment of the alloy deposit. The proportion measured by quantitative EDX shows a proportion closer to 60at% for Pb and 40at% for Bi. Deposit thickness are not known but they were estimated to be at least some hundreds nm by using 30KeV EDX electrons on Pb-Bi deposit.

The specimen was then brought back in air and transported to the mechanical testing device, an electromechanical universal testing machine MTS 20/MH. The tensile test cell was first vacuumed up to  $10^{-5}$  mbar via a turbomolecular pump. Then the tensile testing was performed under the protection of a high purity He cover gas. Heating to 340°C was performed within 2 hours and tensile testing was performed at constant stroke displacement velocity corresponding to a strain rate of  $10^{-4}$ s<sup>-1</sup>.

## Results and discussion

The specimen was observed for fractography analysis in a LEO 1530 FEG-SEM. Both secondary electrons (SE2) and back-scattered electrons (BSE) images are presented. In BSE mode, Pb-Bi appears as white contrast compare to Fe-Cr due to higher Z. In the temperature range of consideration, the usual mode of fracture of this steel takes place by microvoid coalescence.

Multiple cracks are observed on the gauge length in the direction perpendicular to stress (Figure 2-a). Most of them are found in the necking area but some also can be found outside. Therefore crack initiation and propagation does seem to occur after some amount of plastic deformation.

The rupture surface examination indicates a mixed brittle/ductile rupture profile which is characterized by an outer ring of brittle cracks connected by ductile shear lips. Brittle cracking originates from the surface and propagates on several hundreds of  $\mu\text{m}$  in a typical scallop like mode (Figure 2-b). Final fracture occurs by the linking up of nonpropagating cracks.

The inner sides of brittle cracks are all covered by small Pb-Bi spots, leaving large cleavage like area free of liquid metal deposit (Figure 3-a and 3-b). The micromechanism of brittle fracture is therefore mostly transgranular cleavage. Crack branching is indeed very little influenced by the prior austenitic grain boundaries as revealed by chemical etching of microstructure on a transverse cut. However in some instances, cracking seems to be intergranular with respect to martensitic platelets or prior austenitic grain boundary (Figure 4). So a mixed mode of failure is not excluded.

Brittle cracking is only limited by supply of liquid metal at the crack tip as shown by recovery of ductile rupture mode by shear void coalescence (Figure 5). In this experiment, evaporation of metal on the surface provides only a small reservoir of liquid metal remaining as an adherent liquid film on the surface thanks to surface tension and good wetting. Once a crack is initiated, a small amount of liquid metal fills in the crack. As the crack propagates, Pb-Bi is pulled at the crack tip by capillarity and so on until there is no remaining liquid metal. In a typical mechanical testing experiment with surface preparation and a large liquid metal bath of low oxygen activity to prevent re-oxidation, the rupture would be fully brittle due to continuous supply of liquid metal and mechanical properties would be very strongly affected. In the type of experiment conducted in this work, the mechanical properties are affected only by a small but noticeable amount (Figure 6). The tests performed in these conditions lead to the following mechanical degradation: the yield stress is almost unaffected, the ultimate tensile strength (UTS) is lowered by 50 Mpa when the normal UTS is close to 550 Mpa . The total elongation is slightly lowered from 25% to 22%.

Because of the limited supply of liquid metal at the crack tip, this type of experiment does not qualify as a true mechanical test for LME. The degree of embrittlement is dependant upon how much Pb-Bi was deposited on the surface. Nevertheless, it demonstrates that brittle cracking can occur at that temperature provided direct contact is obtained with the liquid metal. We can then infer that LME for martensitic steel does not require specific metallurgical conditions. The notch used in previous studies certainly helps by promoting higher tensile stresses to be reached and concentrating deformation at the surface region. This is a known way of enhancing LME effects but it appears not a necessary condition to evidence brittle cracking as well. One may indeed see the notch effect as a way to promote direct contact because the high stress reached at the notch leads to oxide cracking and promotes intimate contact at the stress concentration point.

The results reported in this paper are in accordance with the existing literature on steel LME [11, 12]. Brittle cracking is observed when intimate contact is obtained and after the specimen has been subject to plastic deformation. These are the 2 phenomenological criteria for witnessing LME. The intimate contact is an experimental requirement. Our results, contrasting with previous reports, show that in mechanical testing in liquid metal environment, one has to deal with the wetting problem. The rupture mode indicates that LME for this type of steel can be interpreted by the adsorption-induced reduction of the bond strength.

## Conclusion

Martensitic T91 steel is prone to LME by Pb-Bi. This behaviour can easily be hindered by the passivation layer of these steels unless special means of oxide removal is used. No special metallurgical state is needed to induce embrittlement. The fracture mode is little influenced by prior austenitic microstructure but seems to be a mix of transgranular and intergranular cracking with respect to martensitic platelets. Prior plastic deformation seems required before cracking can be observed and cracking seems to propagate without initiation incubation time. The martensitic T91 steel in contact with Pb-Bi exhibits all the known facets of LME. This work also indicates that design of Pb-Bi loops with this type of steel should consider LME as a potential risk in general.

## Acknowledgement

J.L. Pastol is kindly thanked for help in using the scanning electron microscope. J.P. Chevalier is kindly thanked for critical reading of the manuscript and fruitful discussion. This work is part of European research program developed for spallation targets and hybrid system. Financial support by the European program MEGAPIE-TEST (FCKW-CT-2001-00159) is gratefully acknowledged.

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Table I: Chemical composition of the steel T91

Element	Cr	Mo	V	Mn	Si	Ni	C	Nb	Fe
Weight%	8.26	0.95	0.2	0.38	0.43	0.13	0.105	0.08	balance

Table II: Main chemical impurities in PbBi

Element	Ca	Hg	S	Fe	Na	Ag	Zn	Al	Ni	Cu
wppm	59	52	35	17	16	14	10	9	4	2

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Figure 1: Typical derived Auger spectra for T91 steel : a) after polishing b) after ion beam sputtering.

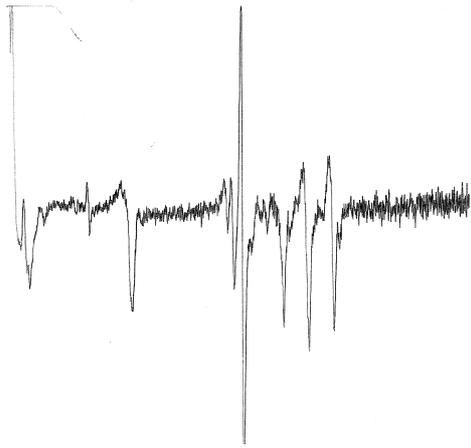
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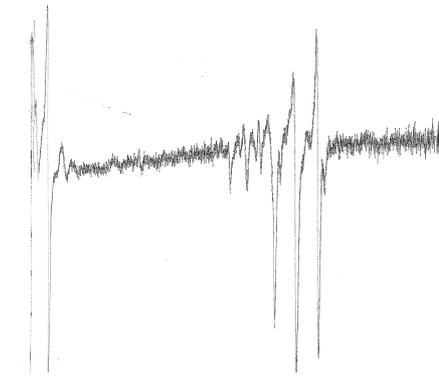
Figure 4: Transverse cut view of a crack arrest area. The microstructure has been revealed by chemical etching. A indicates where crack seems to follow prior grain boundary, B indicates a cleavage area

Figure 5: top view of ductility recovery by lack of supply of liquid metal (SE2 view). A is in a brittle area and B in a ductile area

Figure 6: Tensile curves of T91: reference versus partially embrittled



a)  
Figure 1



b)

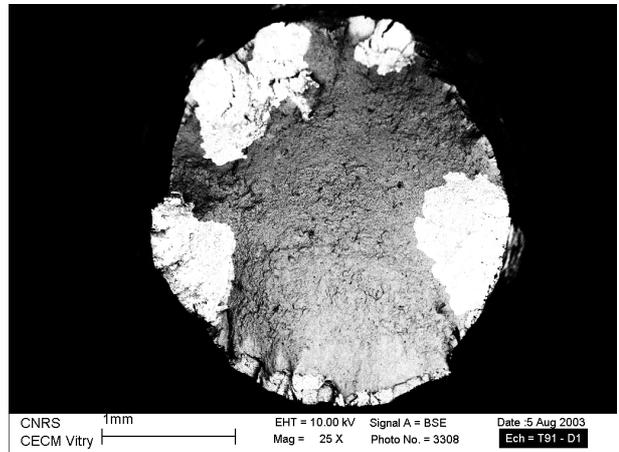
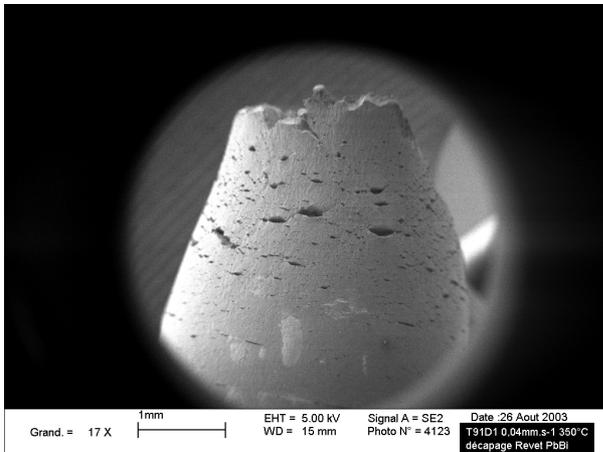


Figure 2

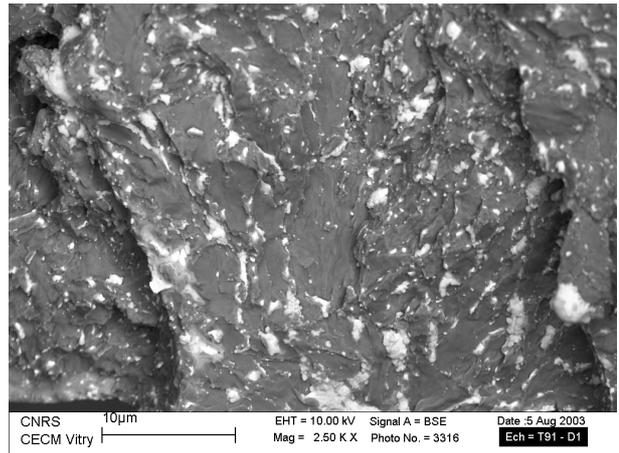
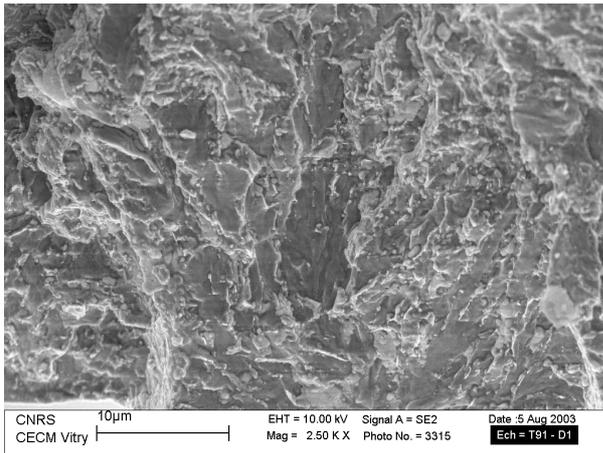


Figure 3

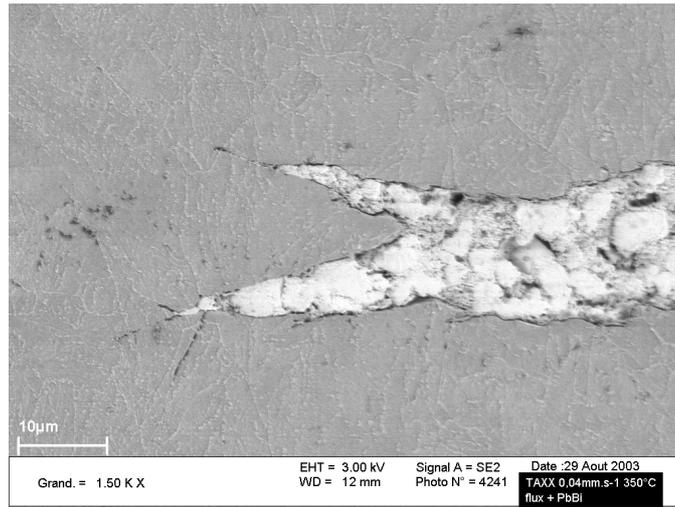


Figure 4

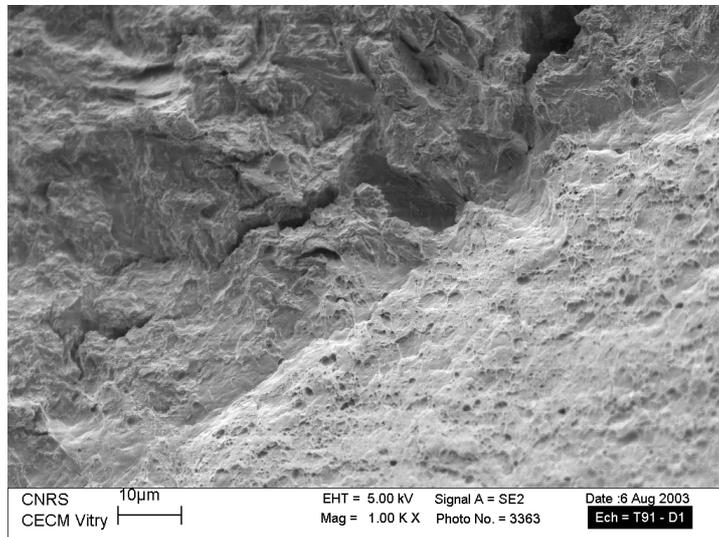


Figure 5

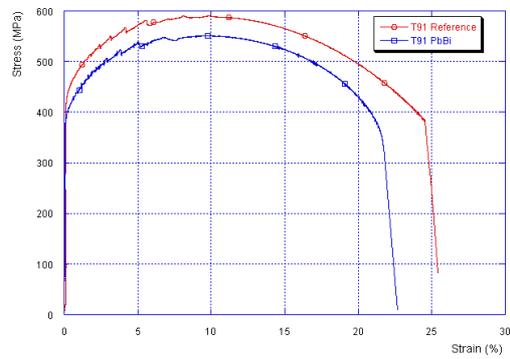


Figure 6