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

T. Auger, G. Lorang
CNRS - Centre d’Etudes de Chimie Métallurgique,
15 rue Georges Urbain
94407 Vitry sur Seine CEDEX

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## Abstract:

Previous studies on T91 steel in its standard metallurgical state do not provide evidence for Liquid Metal Embrittlement (LME) by eutectic Pb-Bi. In this paper, we show 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 of the native oxidized film.

## 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 be exposed to Pb-Bi and will be subject to corrosion and irradiation. LME can also occur if the steel is found sensitive to that environmental effect. 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 LME studies on 91 grade steels with Pb or Pb-Bi concluded that the mechanical behaviour is not affected in its standard metallurgical state but it becomes notch sensitive in this environment 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]. So heat affected zones of welds are critical if no post-weld heat treatment is performed. A similar conclusion was given 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 behaviour [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 steel. It has already been noted that wetting is difficult to obtain on such steel due to the native oxide [13].

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. One of the 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]. However lead contamination can occurs with zinc, which is a known steel embrittler. Chloride cracking can also be expected with such treatment. Here, with the use of physical techniques deposition (PVD) under ultra-high vacuum (UHV), the problems previously mentionned can be avoided.

## 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, furnished 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 $\mu$m 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.

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 |

### Sample preparation

Mechanical testing samples were diamond polished down to 1$\mu$m and washed in acetone using ultrasonic treatment. Afterwards, they were introduced into an Ultra High Vacuum (UHV) surface analysis system ($2.10^{-10}$ mbar). An ion etching cleaning process was applied until the natural oxide superficial 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 ($5.10^{-8}$

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 (Figure1-c), very similar to passive layers formed on stainless steels [9]. Some carbon and chlorine traces are also depicted: they usually originate 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).

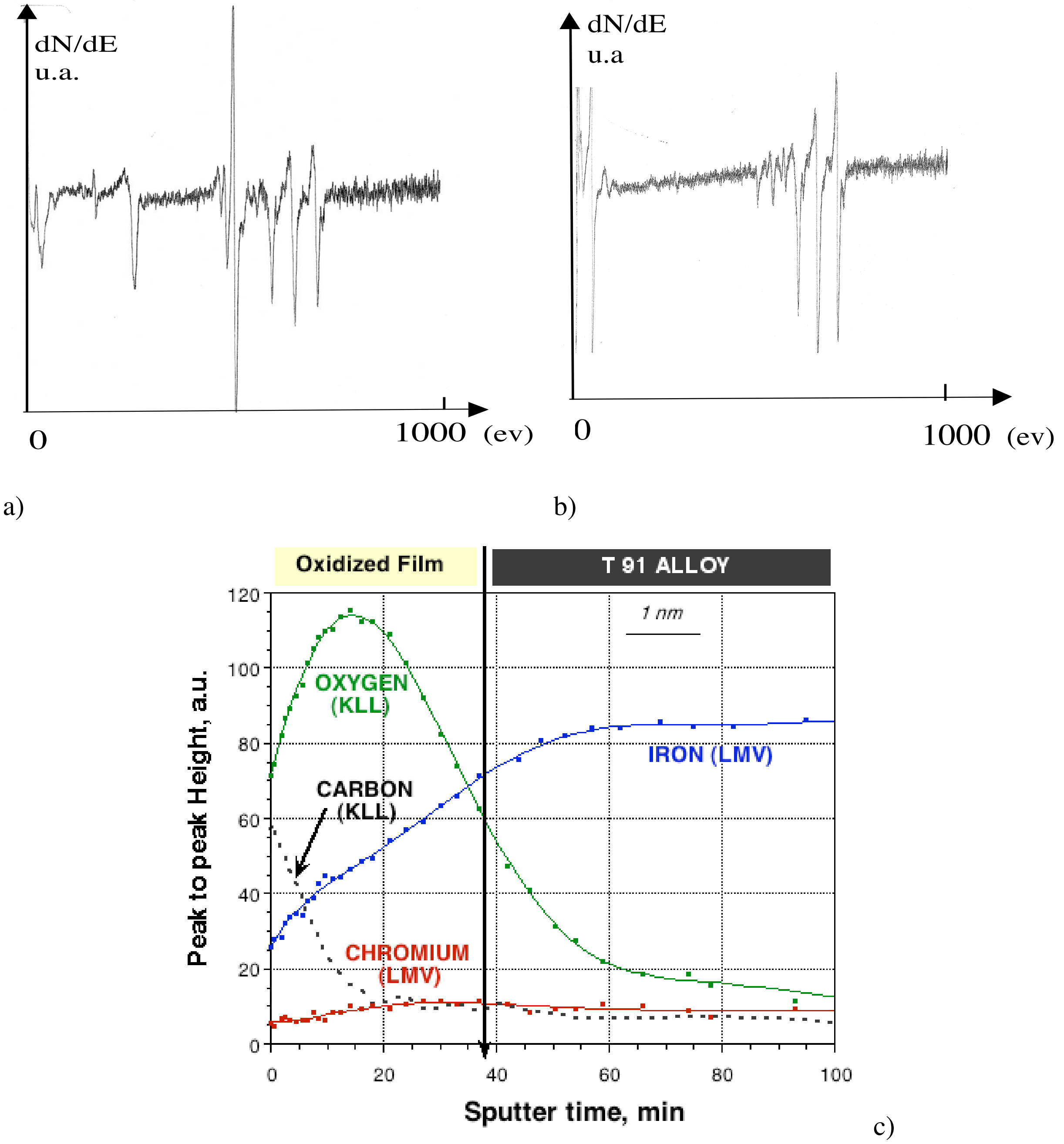


Figure 1 Typical derived Auger spectra for T91 steel : a) after polishing b) after ion beam sputtering c) depth profiling.

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 basket by Joule effect constitutes the source for the metal evaporation towards the gauge closely located onto a transfer rod. According to Honig [10], the vapour pressures of Pb and Bi are of the same order; nevertheless their evaporation rates should lead to a lead enrichment of the alloy deposit. Quantitative EDX performed on the Pb-Bi deposit indicates a proportion close to 60at% for Pb and 40at% for Bi. Deposit thickness is not known but is roughly estimated to be at about a few hundreds nm by using 30KeV EDX electrons.

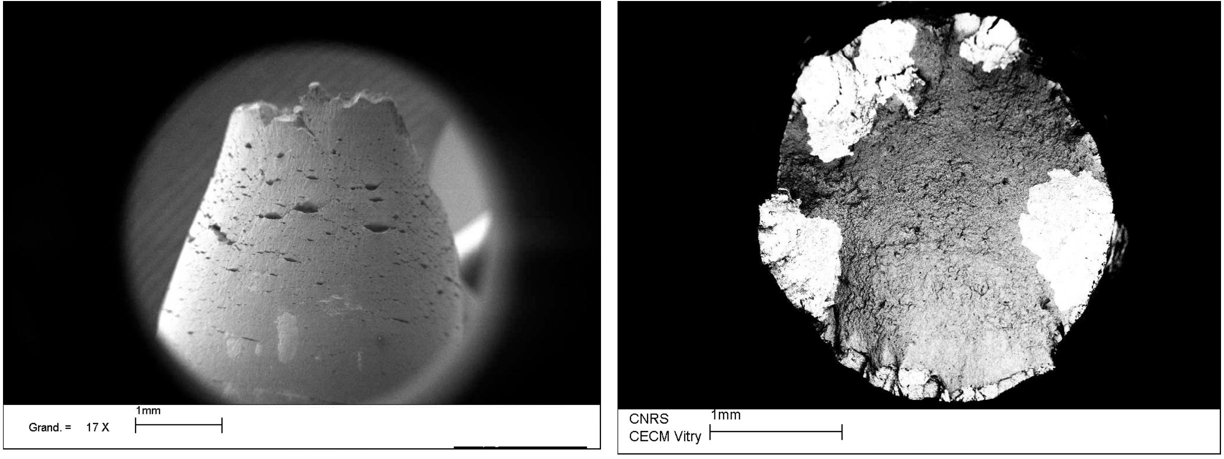
The specimen was then brought back in air and transported to the mechanical testing device, an electromechanical universal testing machine MTS 20/MH. The tensile test cell was pumped up to $10^{-5}$ mbar via a turbomolecular pump. Tensile testing was performed under the protection of a high purity He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

## Results and discussion

Fractographic analysis of the broken specimen is performed 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 proceeds by microvoid coalescence nucleated at precipitates.

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.

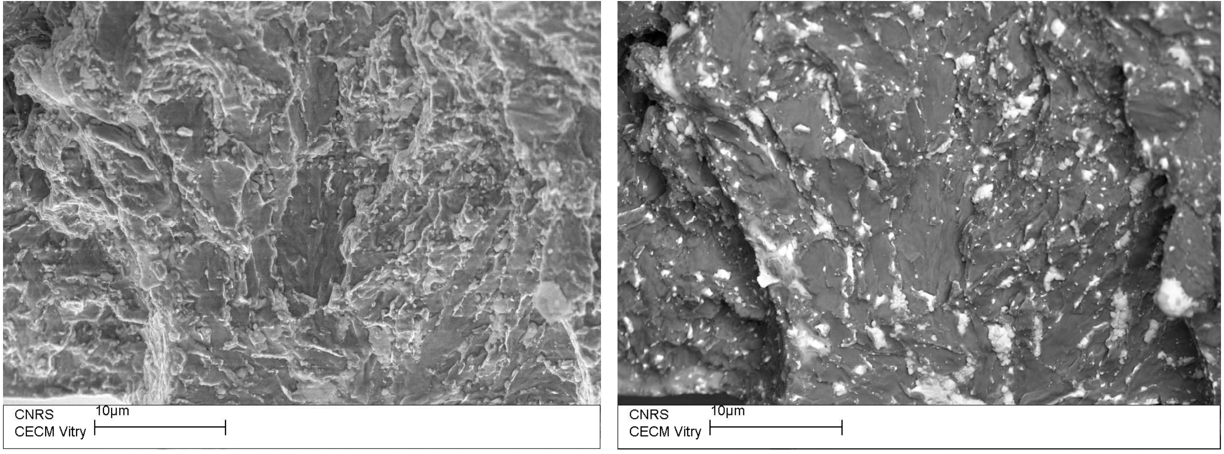
The rupture surface examination indicates a mixed brittle/ductile rupture profile which is characterized by an outer ring of brittle cracks connected by ductile shear lips. Brittle cracking originates from the surface and sometimes propagates on several hundreds of $\mu$m in a typical scallop like mode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



a) b)

Figure 2: View of fracture surfaces a) SE2 view of the cracked gauge length b) BSE top view of specimen fracture showing liquid metal penetration front

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 mechanism 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 (villela reactant). 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.



a) b)

Figure 3: SEM view of an initiation site close to the surface showing quasi cleavage fracture surfaces a) SE2 picture b) BSE picture

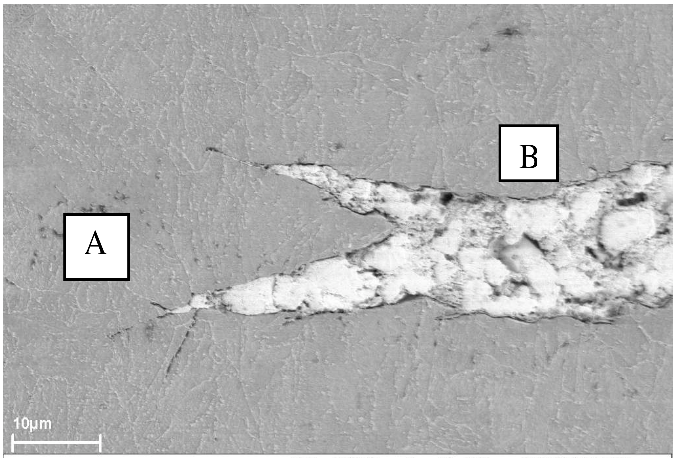


Figure 4: Transverse cut view of a crack arrest area. The microstructure has been revealed by chemical etching. A indicates where crack seems to follow prior grain boundary, B indicates a cleavage area

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).

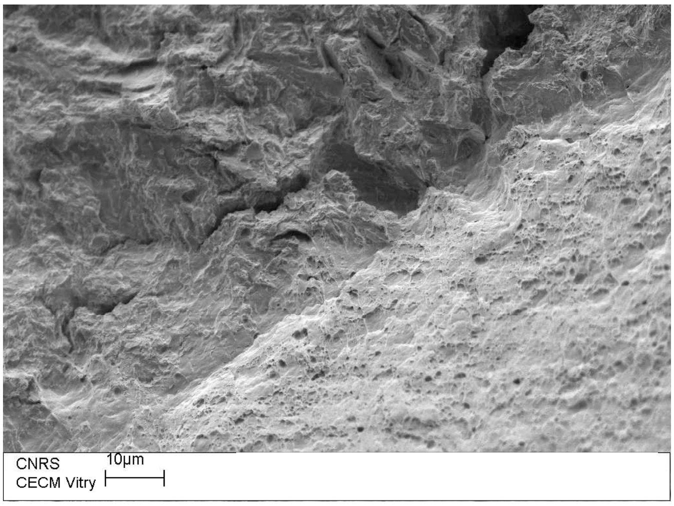


Figure 5: top view of ductility recovery by lack of supply of liquid metal (SE2 view).

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%.

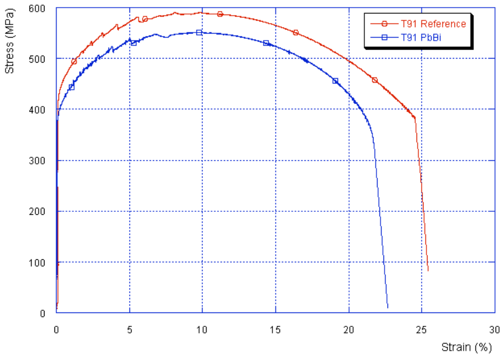


Figure 6: Tensile curves of T91: reference curve versus partially embrittled

Because of the limited supply of liquid metal at the crack tip, this type of experiment is difficult to interpret for mechanical properties degradation. 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 the test 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 as opposed to previous statement [2-4]. 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 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.

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## Bibliography

[1] G. S. Bauer, Y. Dai, S. Maloy, L. K. Mansur and H. Ullmaier, J. Nucl. Mater. 296, Issues 1-3 (2001), 321
[2] A. Legris, G. Nicaise, J.B. Vogt, J. foct, D.Gorse, D. Vançon, Scripta mater. 43 (2000), 997.
[3] G. Nicaise, A. Legris, J.-B. Vogt and J. Foct, J. Nucl. Mater. 296 (2001), 256.
[4] A. Legris, G. Nicaise, J. -B. Vogt and J. Foct, J. Nucl. Mater. 301 (2002), 70
[5] T. Sample, H. Kolbe, J. Nucl. Mater.283-287 (2000), 1336 and references herein
[6] S. Guérin, J.L. Pastol, C. Leroux, D. Gorse, J. Nucl. Mater. 318 (2003), 339
[7] N.K. Batra, J.B. See, T.B. King, Welding research, supp. October (1974), 417
[8] I. Ueda, M. Miyake, M. Kawamura, Trans. Jap. Welding Society, v4, 1 (1973), 119
[9] G. Lorang, M. Da Cunha Belo, A.M.P. Simoes, M.G.S. Ferreira, J. Electrochem. Soc. 141 (1994) 3347
[10] R.E. Honig, RCA Review 23 (1962) 574
[11] W.R. Warke, K.L. Johnson, N.N. Breyer, Corrosion by Liquid Metals, Plenum Press, New York (1970) 779
[12] I.H. Dmukhovs'ka, V.V. Popovich, Materials Science, v29, 5 (1993), 501 and references herein

[13] C. Lesueur, D. Chatain, C. Bergman, P. Gas, F. Baque, J.Phys. IV, 12 (2002) 155