1.3.2 LIQUID METAL EMBRITTLEMENT:
FROM BASIC CONCEPTS TO RECENT RESULTS RELATED TO STRUCTURAL
MATERIALS FOR LIQUID METAL SPALLATION TARGETS

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Abstract
At first, the basic features of LME are recalled (definition, characteristics, embrittling
couples), together with classical experimental features and open questions. Then, a review of
a few very recent results obtained on classical embrittling couples but using new powerful
investigation techniques developed in France is proposed. Second we define LMC. The
"LME- LMC" correlation is postulated. Then we concentrate on the LME-LMC problem
related to the build-up of the Liquid Metal Spallation target in the frame of the MEGAPIE
project. The Russian expertise on LME is briefly mentioned. Then we present some results
obtained in the frame of the "Groupement de Recherche" GEDEON, focusing on steel grade
T91 in contact with lead and lead-bismuth eutectic, in agreement with Russian literature.

Keywords: Liquid Metal Embrittlement, intergranular penetration, Liquid Metal Corrosion,
Lead-Bismuth eutectic, steels, spallation target, ADS.

1. Introduction
One task is to define Liquid Metal (LM) Corrosion, another one to define LM
Embrittlement, because of the intriguing synergy between the stress - strain state and the
environment. One can define LME as a degradation of the mechanical properties of an
otherwise ductile metal (like Cu, Al...) induced by some interaction with LM and mechanical
solicitation. Since its discovery in 1874, embrittlement of structural materials by Lead-
Bismuth was extensively studied, especially in Russia during the 50's for nuclear applications
[1]. Model studies of model systems [2] appeared in the 70's, and continued to attract the
attention of materials scientists over the past 30 years, not disconnected from basic research
conducted on Grain Boundaries (GB) [3]. Now the renewed interest for LME is motivated by
material research programs related to an important component of the park of nuclear reactors
of new generation for the 21st century, namely accelerator driven subcritical reactors (ADS)
for incineration of minor actinides [4-7].

This paper is organised as follows. In section 2, the main characteristics of LME, related
to thermodynamics, morphology and kinetics aspects, are reviewed and illustrated [6-8].
Basic concepts of very recent models are presented [8-18]. Section 3 is devoted LMC, and
relations with LME [19-21]. Note already that models are presented first, at purpose, since
none of them takes into account the environmental effects on the SM/LM interface. In all
cases, defects are only permitted in the GBs, with quasi ideal SM/LM interfaces (smooth at all
scales and free from segregating metallic or metalloid impurities, except the embrittling
atoms). In section 4, susceptibility to LME of iron base alloys is first shortly reviewed.

Then we come to the LME and related LMC studies carried out in the frame of the
“Groupement De Recherche GEDEON” (GEstion des DEchets par des Options Nouvelles),
taking into account the characteristics of the MEGAPIE spallation target [7,20-22]. We
conclude briefly.
2. Liquid Metal Embrittlement

2.1 Main characteristics of LME.

Just as for Localised Corrosion (LC) or Stress Corrosion Cracking (SCC) [8], one distinguishes three phases: nucleation, subcritical growth, and propagation until final rupture with possible crack arrests. Most studies concern the phase of subcritical crack growth. The crack nucleation phase is unknown. Cracking is in general intergranular, scarcely transgranular.

Thermodynamically, LME may concern all SM/LM couples, whatever the phase diagrams (exhibiting mutual solubility or not, forming or not high temperature intermetallic compounds). There are tables collecting the most studied and considered embrittling and nonembrittling SM/LM couples, as the one proposed by Shunk and Warke [9-10]. In our opinion, the famous SM/LM « specificity » is based on non-exhaustive or inadequate criteria... Of course, the most spectacular case is the embrittling penetration of Aluminium by liquid Gallium. Nonembrittling couples can be incorrectly considered either because suitable testing and analysing conditions were not applied or are still missing or because the crack growth rate is so slow or too slow regarding the experiment duration [11].

To illustrate this important point, we reported in Figure 1 results published in 1960 by Rostoker et Coll. [12] It is well known that Cu is severely embrittled by Bi. Shall we conclude that Cu is rather immune against LME in Pb? Shall we not better suppose that the embrittling criteria were not fulfilled under the operating conditions of Figure 1?

![Figure 1](image)

Let us note that rare gases, like Argon, can be also embrittling. The only difference is that the crack propagation rate, \( v_{\text{crack}} \), in Cu under Argon cover gas is three orders of magnitude slower than in Bismuth!

For real SM/LM couples, surface heterogeneities constitute a source of crack initiation sites (as for LC!). A simple-minded scheme including parameters favouring (LM, stress \( \sigma \)) and hindering (oxide layer) crack propagation is shown here. Are missing the SM strain state and all chemical impurities in both phases. Rebinder first proved that the contact with LIM reduces the surface energy, now \( \gamma_{SL} \) if perfect wetting.

The Griffith criterion gives the critical stress \( \sigma_c = \left[ 2E \frac{\gamma_{SL}}{\pi c} \right]^{1/2} \) for crack growth of size \( c/2 \). Using \( K = \left[ \pi c/2 \right]^{1/2} \), we define the critical stress intensity factor \( K_{IC} = \left[ 2E \gamma_{SL} \right]^{1/2} \). So we justify qualitatively the huge difference in susceptibility to LME of Cu/Bi with respect to Cu/Pb.
Crack propagation gives rise to the opening of "fresh" surfaces at crack tip. The crack propagation rate is determined by the competition between the oxidation kinetics in the crack tip area and the kinetics of penetration of the embrittling (LM) atoms, once defined the metallurgical conditions (stress-strain state).

There are different crack morphologies, depending on the SM/LM system (nature and purity), environmental, metallurgical and mechanical testing conditions: Mullins groove, finger-like, or rather narrow channels as the one displayed in Figure 2 [13].

Over a depth of order 100 μm, the crack width is invaded by Bismuth, leading to a Bi film wetting the parallel channel walls. Beyond, Bi is no longer observable, while the crack becomes narrower, of submicronic, then nanometric width with approaching the crack tip area. Note that Ni is clearly embrittled far ahead of the micrometric film!

Impact broken Ni specimens were analysed in situ within an Auger spectrometer which allowed to reveal the presence of Bismuth on fracture surfaces and to quantify the number of Bi layers present in the GBs.

Rabkin addressed the question of how the embrittling atoms are supplied in the crack tip zone and beyond [14]. Writing the width of the steady-state diffusion zone ahead of crack tip as \( l = \frac{D_{GB}}{v_{crack}} \) gives \( l \approx 10^{-12} \text{ cm} \) for \( v_{crack} \approx 0.1 \text{ cm/s} \) and \( D_{GB} = 10^{-14} \text{ cm}^2/\text{s} \) at about 0.3 Tm (Tm designates the SM melting temperature) which is unrealistic.

To make this value acceptable, Rabkin suggested first that a tensile stress might accelerate GB diffusion. The author also assumed that the driving force for "diffusion" could be affected too.

Finally, a pre-melted GB was assumed, consistent with a sufficient diffusivity (10^2 cm^2/s) to supply the embrittling atoms in the GB, and allowing for intergranular cracking.

The question of applied stress is also a matter of debate. Scientists studying wetting and intergranular penetration often consider tensile stress is not a prerequisite parameter for occurrence of LME. Definitions of LME can be found in the literature where \( \sigma \) tends to zero, the prominent role of the LM embrittling phase being emphasized. Al/Ga is the best couple to the purpose of validating such models of LME.
Of course it is known that LME occurs at applied stress much lower than the yield stress (Fig 1). However, the above Figure 4 enlightens the important role of the stress-strain state regarding susceptibility to LME of Al put into contact with a Gallium drop. Note that the stress-strain state influences the morphology of the fracture.

With stress, the tensile components are in the Ox direction. On the contrary after stress removal and elastic relaxation, the residual tensile stress is in the Oy direction which explains the geometry of fracture seen in Figure 4. We have also chosen to present this experiment since Al/Ga is the perfect example of embrittling couple at zero applied stress!

Powerful techniques are now available to study LME. First, synchrotron radiation X-ray microtomography recently proved to be a very useful tool for investigating propagation paths and kinetics of the "embrittling" elements in a metallic polycrystal [15]. Second, High Resolution Transmission Electron Microscopy (HRTEM) and related analysis techniques permits to attain elementary defects in GBs. It could be of great help to understand their influence on penetration of the embrittling elements and on intergranular crack advance [7].

Contrary to an opinion found in recent literature [16], we would like to emphasize that LME can be observed over a wide temperature range, not determined by the melting temperature of the "embrittler" ($T_{m,E}$) and confined in a narrow range given by $T_{m,E} \pm 50^\circ$C. This point will be confirmed in Section 4 where susceptibility to LME of steel grade T91 in Pb-Bi eutectic will be specifically treated.

Recent modeling of LME take into account some ingredients of intergranular cracking discussed above and try to explain the crack morphology and its kinetics of propagation. The role of externally applied stress is not explicitly included.

It would have been surprising that the Mullins groove requiring thermodynamic equilibrium conditions in the crack (see scheme opposite) describes satisfyingly its morphology. However, this theory of thermal grooving allows to define an equilibrium dihedral angle $\theta_0$ using: $2 \gamma_{SL} \cos(\theta_0/2) = \gamma_{GB}$

On can easily think how difficult to measure the dynamic wetting angles on crack walls and $\theta_d$ at crack tip, once remarked that an acute measurement of the time dependent curvature gradients are a key factor for modeling crack propagation.

Glickman et Coll. [17] proposed that the non zero dynamic concave angle that develops at crack tip is responsible for an inward driving force $F$:

$$ F \propto \gamma_{GB} \left[ 1 - \cos(\theta_0/2) / \cos(\theta_d/2) \right] $$

with the above definitions of $\theta_0$ and $\theta_d$ and for the transport of "embrittling atoms ahead of crack tip, in the GB".

On the other hand, Chatain et Coll. [18] developed another approach, emphasizing the role of structural defects in the GBs, especially facets, and allowing to predict the observed linear LM penetration rate as well as the crack morphology found remarkably time-independent in the literature.

3. Liquid Metal Corrosion (LMC)

3.1 definition and application to 9%Cr martensitic steels

LMC means passive film growth (~nm) and thickening (~µm) on an oxidisable metallic alloy followed by generalised or localised corrosive attack. In principle, self-healing of locally depassivated area (Pits) may be obtained by active oxygen control in the LM bath.

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1 We do not develop here the arguments given by the authors to iterate the process. Neither do we comment the fact that this process implicates high stress. After Glickman, wetting induced surface roughening of GBs will make easier point defect production and decrease $\gamma_{SL}$. 

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Recent studies, using dedicated devices like COXCIMEL with electrochemical oxygen control in LM bath and suitable cover gas \[7-19-21\], have shown that over a wide range of oxygen contents going from highly reducing \((-10^{10}\text{ wt.}\%\text{O}_2\)) to highly oxidizing conditions \((\sim10^{18}\text{ wt.}\%\text{O}_2)\), the steel surface of the 9%Cr pre-selected steels for the MEGAPIE spallation target and future ADS is always found a priori oxidised, and poorly wettable by LM (Fig. 5), in agreement with classical thermodynamics and Ellingham Diagrams.

![Figure 5](image)

**Figure 5.** (Left) Diagram showing the oxidation conditions used in IPPE-Obninsk by Markov et coll. \[7\] giving rise to surface oxide films, whose protectiveness and wettabiliy by LM should be already initially function of the temperature and oxygen content. (Right) SEM micrograph showing a top view of oxidised T91 steel surf. after 15 days ageing above a stagnant Pb bath under highly reducing conditions in COXCIMEL set-up revealing Pb droplets and the bad wettabiliy of the oxide surface film, *After V. Ghetta et Coll [19-21]*

### 3.2 Relation LMC - LME: case of 9%Cr martensitic steels

It was also shown that one month ageing under highly reducing conditions gives rise to surface pitting and roughening. Less known, ageing under similar conditions in LM causes also appearance of porosities in the T91 steel in bulk \[7\]. It is argued that pits, pores, and roughness induced by exposure of T91 steel to Lead might be very detrimental regarding susceptibility to LME. Note that such corrosive degradations do not require long-term ageing (just a few weeks !), and that exposure to lead-bismuth eutectic could possibly accelerate this ageing process and affect resistance to LME. This is pure conjecture!

According to the Kamdar criterion that intimate SM/LM contact at atomic scale is a necessary condition for occurrence of LME, it could be tempting to suppose:
- that "unaged" steel specimens, covered with an oxide film in the very initial protective stage of LMC, are not prone to LME;
- but that ageing in LM causes degradation of resistance to LMC, taking the form of "pits - pores and roughness" and thus might increase substantially the susceptibility to LME.

This is what we call the "LMC-LME" correlation. After long-term ageing in LM \[21\], in any case, the SM/LM contact will be macroscopically recovered possibly permitting LME.

### 4. Susceptibility to LME of 9%Cr martensitic steels in liquid Lead alloys

#### 4.1 from Iron Armco to 9%Cr martensitic steels

Even a non exhaustive review of the Russian literature from the 60's gives an idea of the considerable amount of knowledge already existing as concerns susceptibility to LME of both model systems and real systems, like steels in contact with Lead, Bismuth and their alloys. Metallurgical and environmental criteria were already studied. This point is illustrated below.

Susceptibility to LME was known to be dependent on i) surface state, ii) metallurgical parameters like grain size, iii) environment meaning temperature and chemistry of the contacting phase. Briefly, susceptibility to LME is maximized around 350°C for polished specimens of iron or iron-base alloys of large grain size. The steel microstructure as a whole (lath structure, precipitates...) is determining. The welding effect on LME was studied.

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4.2 Resistance to LME of 9%Cr martensitic steels in Lead-Bismuth: some recent features

Today, 9Cr-1Mo mod. steel grade (T91) is studied in the frame of both ADS and LM spallation target projects [4,7,22]. In order to validate the “T91 steel/Pb-Bi eutectic” system for the target window and LM respectively, one has to verify the LMC and LME resistance without and under the specific irradiation conditions of the MEGAPIE spallation target. We concentrate here on some aspects of the problem without irradiation. The irradiation effects including Hydrogen and Helium effects will be the treated with LiSoR experiment and in fine with the MEGAPIE target.

One has to check the LME resistance under the more severe environmental conditions and damageable metallurgical conditions. From the tensile behaviour of T91 steel in LM, we deduce immediately the energy to fracture (calculated as the area under the load vs. cross-head displacement plots).

From the metallurgical point of view, one can combine suitable heat treatment and notch effect: the tensile tests are carried out in air as function of the temperature of the stagnant LM bath (Fig. 9.a). This gives the ductility trough of Fig. 9.b [7].

On the other hand, keeping the steel in its standard metallurgical state, we may vary the environmental conditions (vacuum or hydrogenated helium), temperature and mechanical test conditions. The LME effect is net by comparing the tensile behaviour of notched T91 steel specimens in Pb-Bi eutectic under hydrogenated helium with a reference in vacuum (Fig. 9.c).

Recalling that 9%Cr martensitic steels were selected as the best compromise between fabricability and resistance to severe irradiation conditions and lead alloys environment, as stated in the GEDEON Material research program, these results are considered with special attention [4,7].
**Figure 9.**
a) Exemplary load vs. cross-head displacement plot with heat-treated T91 steel at 350°C in air or contacting lead in air; b) Corresponding ductility trough for T91 steel after hardening heat treatment in [350-450°C] temperature range; After G.Nicaise et Coll. [7]; c) Same as in a) for T91 steel in standard metallurgical state exposed to vacuum and to Lead-Bismuth eutectic at 350°C under He-4%H₂ [22].

**Figure 10.** Energy to fracture vs. crosshead displacement rate for notched T91 steel (in standard metallurgical state) tested in vacuum (open symbols), under He-4%H₂, and in Pb-Bi under He-4%H₂ (full symbols) at 300°C, 350°C and 400°C. Rupture facies obtained on notched T91 steel specimens in Pb-Bi eutectic under flowing He-4%H₂ for a cross-head displacement rate of 1.6 10⁻⁶ mm s⁻¹ at 300°C (left) and at 400°C (right).

As seen in Figure 10, resistance to LME is degraded not only by applying suitable hardening treatment but just by choosing a suitable combination of cross-head displacement rate, temperature and cover gas. Apparently, the embrittling effect of Pb-Bi is made clearer under flowing He-4%H₂. The role of hydrogen, at the SM/LM interface or in bulk steel is

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outside the scope of this paper. Even at low magnification, in otherwise identical conditions, we observe a significant change in the rupture faciés with increasing temperature. At 300°C, the facies is ductile (equiaxed dimples). At 400°C, the evolution is net, crack nucleation occurred in a single area.

Other studies have shown a substantial acceleration of creep for T91 steel contacting Pb-Bi under pure H2, not observable in the absence of the LM phase. This result suggests that the LM induced roughened surface is a perfect source for points defects (vacancies...), detrimental for both tensile and creep behaviour. From this point of view, one can conjecture that a rigorous control of the oxygen content in the spallation target should be welcome to avoid “pits, pores and roughness”!

Let us mention that we were not concerned here by the influence of radiation damage and production of spallation elements (especially helium and hydrogen) that will harden and embrittle the steel. Last, the problem of He embrittlement, of H embrittlement, of (He+H) then finally of (He+H+LM) embrittlement is evoked incidentally here. It will be a challenge for the next coming years and the new generation of nuclear reactors.

4. Conclusions
In this paper, well-known characteristics of LME and LMC are recalled. Concerning 9%Cr martensitic steels proposed for the spallation target of future ADS, we have shown that long-term exposure of metallic alloys to LM decreases the resistance to LMC, giving rise to “pits – pores” and surface roughening, and could be somehow responsible for a LME effect, not a priori expected with these steels. Work is in progress to “quantify” these preliminary results before beginning mechanical tests under irradiation in LiSoR experiment.

Acknowledgements

Financial support of French « Groupement de Recherche GEDEON », of TECLA and MEGAPIE-TEST programs founded by the EU 5th fwp are acknowledged. Thanks are due to all Colleagues of the CNRS-Dpt.SC and IN2P3 involved in these programs. DG thanks especially V. Ghetta for fruitful discussions.

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