Twin boundary-accelerated ferritization of austenitic stainless steels in liquid lead-bismuth eutectic

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Abstract

Exposure of austenitic stainless steels to liquid lead-bismuth eutectic with low concentration of dissolved oxygen typically results in selective leaching of highly-soluble alloying elements and ferritization of the dissolution-affected zone. In this work, focused ion beam, transmission electron backscatter diffraction and scanning transmission electron microscopy were utilised to elucidate early-stage aspects of the dissolution corrosion process of cold-worked austenitic stainless steels exposed to static, oxygen-poor liquid lead-bismuth eutectic at 450°C for 1000 hours. It was found that deformation-induced twin boundaries in the cold-worked steel bulk provide paths of accelerated penetration of the liquid metal into the steel bulk.

Keywords: steels; liquid metal corrosion (LMC); focused ion beam (FIB); electron backscattering diffraction (EBSD); scanning/transmission electron microscopy (STEM)

Heavy liquid metals (HLMs) are proposed as heat transfer media for nuclear power, neutron spallation sources and concentrated solar power (CSP) applications. The lead-bismuth eutectic (LBE) is a cost-efficient HLM characterized by high thermal conductivity, reasonable heat capacity, good neutron yield, low neutron cross-section and low chemical reactivity with other coolants [1], facts that make it a good high-energy heat transport medium [2-4]. A challenge in

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4 using LBE as coolant in Gen-IV lead-cooled fast reactors (LFRs) and/or spallation target in
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6 accelerator-driven systems (ADS) [5], such as the flexible fast-spectrum irradiation facility
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8 MYRRHA, is its inherent corrosiveness towards many candidate nuclear grade steels. The
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10 strategy for mitigation of undesirable liquid metal corrosion (LMC) effects is based on three
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12 pillars for the MYRRHA system: moderate nominal operation temperatures ($< 450^{\circ}\text{C}$), active
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14 oxygen control and in-depth understanding of the LMC mechanisms. Active oxygen control
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16 relies on the addition of controlled amounts of oxygen to the HLM coolant to form a protective
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18 oxide scale on the steel surface [6-11]. In complex heat transport systems, however,
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20 maintaining the targeted oxygen level constant everywhere in the system is difficult and the
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22 establishment of oxygen-depleted zones of static HLM will result in dissolution attack, since the
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24 formation of a passivating oxide is suppressed [12]. Moreover, the oxide scale is not fully
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26 protective and sites of locally-accelerated dissolution might develop in various steels under the
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28 oxide scale [13,14]. Since detailed microstructure-LMC relationships have not been previously
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30 established, this work addresses the interplay of the microstructure of cold-worked 316L
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32 austenitic stainless steels, the MYRRHA candidate structural material, with early stages in the
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34 dissolution corrosion process. Advanced electron microscopy techniques, such as transmission
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36 electron backscatter diffraction (t-EBSD) and scanning transmission electron microscopy
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38 (STEM), are deployed in a focused ion beam (FIB) instrument to bring new insight into the role
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40 of deformation-induced twins in the dissolution corrosion behavior of cold-worked 316L steels.
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42 The importance of this work lies in the identification of a novel mechanism of accelerated
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44 degradation of cold-worked austenitic stainless steels in contact with oxygen-poor LBE.
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48 Solution-annealed and cold-worked 316L austenitic stainless steel heats were simultaneously
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50 exposed to oxygen-poor, static liquid LBE at 450°C for 1000 h. The steel discussed here
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52 (316LH1) was solution-annealed at 1060°C for 4 h, water-quenched and cold-deformed into a
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54 rod ($\varnothing$ 10 mm) by OLARRA Aceros Inoxidables, Spain. The exact cold working parameters are
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56 not available. The steel chemical composition in mass% is: 0.028% C, 0.34% Si, 1.85% Mn,
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58 0.033% P, 0.027% S, 16.7% Cr, 10.1% Ni and 2.06% Mo; the balance is Fe. The cylindrical 316LH1
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60 steel specimen ($\varnothing$ 6 mm, length 15 mm) was connected by screw threads with specimens made
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of different 316L heats, finally polished with 3 μm diamond paste and cleaned with ethanol and acetone prior to LMC testing.

The LMC test setup (inset drawing, Fig. 1) consisted of a stainless steel autoclave with an inner alumina liner to prevent direct contact of the autoclave walls with the LBE bath (~5 kg LBE). Temperature and LBE oxygen concentration were monitored using a thermocouple (type K) and an electrochemical oxygen sensor ($\text{Bi}/\text{Bi}_2\text{O}_3$ reference electrode), respectively. Constant flow (20 ml/min) of a reducing gas ($\text{Ar}-5\%\text{H}_2$, HYTEC 5, Rapid Industrial Gases Ltd.) ensured low LBE oxygen concentration. The specimens were introduced in the LBE bath once its oxygen content dropped below 10^{-8} mass% to suppress steel oxidation that would delay the occurrence of LBE dissolution attack. Figure 1 shows the temperature and LBE oxygen concentration profiles during testing.

After exposure, sample cross-sections were ground and polished to final finish with 1 μm diamond suspension. Scanning electron microscopy (SEM; JSM-6610LV, JEOL) guided the identification of interesting features for further investigation by means of t-EBSD and STEM. A dual beam FIB (Quanta 3D FEG, FEI), equipped with energy-dispersive X-ray spectrometer (EDS; X-Max^N 20, Oxford Instruments), EBSD detector (NordLysNano, Oxford Instruments) and STEM detector (FEI), was used for foil fabrication and imaging. Platinum was deposited on the area of interest prior to ion milling. Combining SEM/EDS, FIB, t-EBSD and STEM in the same instrument has proven to be extremely time-efficient, while providing the needed resolution to elucidate the early stages of LBE penetration into cold-deformed 316L stainless steels.

SEM revealed the presence of thin lines of LBE penetration into the steel up to a maximum depth of 40 μm (Fig. 2b). These features were not perpendicular to the outer steel surface, but changed orientation within the dissolution-affected zone. Their overall appearance suggested an interplay between the local microstructure of the cold-worked steel and the mechanism of LBE ingress. In solution-annealed 316L steels, the ingress of LBE into the steel starts typically by the preferential attack of grain boundaries. Intergranular LBE attack is followed by the selective leaching of highly-soluble steel alloying elements, i.e. nickel (Ni), manganese (Mn) and

chromium (Cr). Grains that underwent selective leaching are eventually consumed by the slow dissolution of the Fe-based grain residues. On the other hand, the dissolution corrosion process in cold-worked steels as the 316LH1 appears different, since liquid LBE penetrates into both grain boundaries and line-like features (Fig. 2a). This implies that linear LBE penetrations are an additional path of preferential LBE ingress into the steel.

FIB was deployed to fabricate thin foils from select areas for further analysis by t-EBSD and STEM. The FIB cross-section of Figure 2c shows three pairs of closely-spaced (0.3-0.8 μm) lines of LBE penetration. While Figure 2b gives a two-dimensional impression of the three-dimensional reality, Figure 2c allows the in-depth observation of the corroded specimen. The first important remark is that the 'lines' of LBE penetration are, in fact, planes extending for more than 10 μm below the cross-section of Figure 2b. The transmission electron microscopy study of these closely-spaced planes showed that they are deformation twin boundaries and the twinning plane is the $\{111\}$, which is typical for an *fcc* metal [15]. Such micro-twins are produced in large numbers during the cold deformation of austenitic stainless steels and have been previously observed in heavily (40%) cold-worked 316 stainless steels [16].

Figure 2d shows the thin foil after it was lifted out, fixed on a copper grid and thinned to electron transparency. The deformation twin boundaries in Figure 2c are still clearly visible and decorated by LBE traces. A very narrow LBE penetration at the lower right-hand side of the thin foil was investigated by STEM, which revealed the extension of the twin boundary guiding the LBE ingress beyond the termination of the LBE penetration (inset, Fig. 2d). t-EBSD showed a crystal tilt between 59.89° and 59.94° (Fig. 4b), indicating a $\Sigma 3$ twin boundary at each site of accelerated LBE penetration. It is, therefore, reasonable to assume that such boundaries enable the LBE ingress into the steel. In literature, studies evaluating twin boundary diffusion were mainly done on copper and it has been stated that (111) twin boundaries reduce the vacancy migration energy by $\sim 10\%$ compared to the perfect lattice [17,18]. Further reduction ($\leq 50\%$) in the vacancy migration energy has been predicted for interfaces, such as (112) twin boundaries, that are characterized by greater structural distortions in the atomic environment of the vacancy migration path; incoherent twins were also reported to enhance diffusion [17]. No dedicated theoretical work has been performed on Pb or Bi diffusion along twin boundaries in

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4 stainless steels, but the accelerated LBE penetration observed here suggests that deformation-
5 induced twin boundaries foster Pb and Bi penetration into the steel.
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9 Figure 3 shows STEM, SEM/EDS and EBSD data acquired from a steel micro-volume enveloped
10 by a pair of deformation twin boundaries. STEM reveals the presence of LBE residues and
11 micro-cavities at the twin boundaries (Fig. 3a), while EDS elemental mapping shows that the
12 micro-volume between twin boundaries has undergone selective leaching of Ni and Cr, which
13 enriched it in Fe compared to the unaffected steel (Figs. 3b-3d). EDS analysis showed selective
14 leaching of manganese (Mn) as well, as shown in the EDS line scan across a typical set of
15 ferritized grains formed at twin boundary junctions (Fig. 3f). Since Ni and Mn are the principal
16 austenite stabilizers [19], their preferential removal by LBE results in ferritization of the
17 dissolution-affected zone, a phenomenon already documented for 316L stainless steels
18 exposed to LBE [20,21] and here confirmed by t-EBSD (Fig. 3e). The phase map of Figure 3e
19 demonstrates that only the steel micro-volume enveloped by the deformation twin boundaries
20 is ferritic (*bcc* structure), while the unaffected steel matrix surrounding this micro-volume
21 remains austenitic (*fcc* structure). Ferritization due to selective Ni removal from austenitic
22 stainless steels has also been reported in liquid mercury [22], lithium [23] and lead-lithium
23 [24,25]. The propagation of dissolution-induced ferritization leaves significantly smaller grains
24 in its wake compared with the size of the parent grains (Fig. 2c), suggesting that the dissolution
25 process is aided on the micrometer scale by the presence of low misorientation angle sub-grain
26 boundaries that could be more susceptible to LBE attack than the grain bulk.
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44 The selective leaching of Ni, Mn, Cr is driven by the greater solubility of these elements in liquid
45 LBE when compared to the solubility of Fe. Martinelli et al. [26] has experimentally assessed the
46 maximum solubility of pure Ni in LBE to be ~2.42 mass% at 450°C. Gossé [27] has performed a
47 thermodynamic assessment of the Ni, Cr and Fe solubility limits in liquid LBE in contact with the
48 $\text{Fe}_{0.71}\text{Cr}_{0.18}\text{Ni}_{0.11}$ model alloy, which is compositionally similar to the 316LH1 steel. He found that
49 Ni has the highest solubility, Cr has 10^2 times lower solubility than Ni in the 227-727°C range
50 and Fe has 10^3 times lower solubility than Ni at 227°C, this gap reducing with temperature. The
51 Ni, Cr and Fe solubility at 450°C, calculated using equations (29), (26) and (27) in Ref. [27], is
52 6.37×10^{-3} , 4.01×10^{-5} and 3.51×10^{-6} mass%, respectively.
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Ferritization of the dissolution-affected zone entails the phase transformation of austenite to ferrite, which is accompanied by an atomic volume increase as the close-packed *fcc* structure (4 atoms/unit cell) changes into the less dense *bcc* structure (2 atoms/unit cell). For a lattice parameter of $a = 3.598 \text{ \AA}$ [16] for austenite (7.964 g/cm^3) and $a = 2.867 \text{ \AA}$ [28] for ferrite (7.870 g/cm^3), the atomic volume during ferritization increases by 1.19%. Albeit limited, the expansion of a ferritized steel micro-volume will increase the stress intensity in its immediate vicinity and will 'open' the twin boundary that enabled LBE ingress (Fig. 4c). In support of the above, t-EBSD phase mapping of thin ($\sim 0.05 \text{ }\mu\text{m}$) laths (*fcc*) shows a lath misorientation of $\sim 60^\circ$ relative to the austenitic (*fcc*) steel matrix (Fig. 4b), suggesting they are twin crystals; moreover, the ferritized (*bcc*) fraction of a twin lath is wider ($\sim 0.15 \text{ }\mu\text{m}$) than the original twin width (Fig. 4a).

Since dissolution corrosion involves the progressive replacement of the steel by LBE (Figs. 2a-2b), it is unavoidably accompanied by a loss of the load-bearing capacity of the dissolution-affected zone. Since LBE replaces all steel parts it consumes, the origin of the cavity-like gaps observed in Figure 2c merits commenting. The relatively easier LBE removal by the ion beam compared to the steel during sample manufacturing is probably a rather limited effect at the ion beam grazing incidence angle. Gaps in the vicinity of twin boundaries might be partly associated with the expansion of ferritized grains that force these boundaries to open (Fig. 4c). The fact that these gaps are intermittently devoid of LBE also suggests that they might have formed during the solidification process. In fact, LBE solidification forms a mixture of phases β (Pb_7Bi_3) and γ (Bi with 0.4% Pb), while the post-freezing transformation of the close-packed β -phase (*hcp*; 11.17 g/cm^3) into the less dense γ -phase (*rhombohedral*; Bi: 9.747 g/cm^3) results in expansion of LBE residues [29]. For LBE-cooled reactors, post-freezing LBE expansion will only occur after the final plant shutdown prior to decommissioning, but helps to explain the crack-like gaps.

Considering the importance of liquid metal embrittlement (LME) in LBE-cooled nuclear systems, one might speculate on the possible susceptibility of 316L austenitic stainless steels to LME due to dissolution-induced ferritization. So far, LME has been reported for ferritic/martensitic steels in contact with oxygen-poor LBE [30,31], but never for austenitic stainless steels. Since an important condition for LME, i.e. the intimate steel/LBE contact at the absence of oxide scale

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4 barriers, is fulfilled in the ferritized dissolution-affected zone, brittle crack formation in this
5 zone might be possible under an externally-applied load. The formation and propagation of
6 such cracks have been associated with 1.4571 austenitic stainless steel tube ruptures in the hot
7 leg of the CORRIDA LBE forced convection loop; however, brittle cracks are typically arrested in
8 the ductile, LME-immune austenitic matrix [20]. Further research is required to confirm the
9 possible synergy of LMC with LME in stainless steels. The observed mechanism of accelerated
10 ferritization of cold-worked austenitic stainless steels concerns nuclear fission (Gen-IV LFR),
11 fusion and CSP systems using Pb alloy coolants (Pb, Pb-Bi, Pb-Li), if full coverage of a protective
12 oxide scale is not guaranteed. Similar degradation effects might occur in other coolants (e.g.
13 molten salts) as well, necessitating the further detailed investigation of such effects in various
14 coolant/material systems. Possible mitigation strategies besides the formation of protective
15 passive films, such as coatings and/or surface alloying, must also be explored for system-
16 specific protection in service.
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32 In this work, FIB, t-EBSD and STEM were used to investigate the early stages in the dissolution
33 corrosion process of cold-worked 316L stainless steels exposed to static, oxygen-poor LBE for
34 1000 h at 450°C. Deformation-induced twin boundaries provided paths of accelerated LBE
35 penetration into the bulk steel, while LBE penetration was followed by the selective leaching of
36 the austenite stabilisers (Ni, Mn) and the ferritization of steel areas around the twin structure.
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FIGURES

Figure 1. Temperature and LBE oxygen concentration profiles and drawing of the test setup. OS = oxygen sensor; S = specimens; T = thermocouple; GBT = gas bubbling tube; AL = alumina liner; SSA = stainless steel autoclave.

Figure 2. SEM images showing (a) LBE penetration along twin boundaries and ferritized grains (crosses) at twin boundary junctions. (b) LBE attack under a solidified LBE droplet; the magnified inset shows the FIB thin foil vicinity. (c) The FIB cross-section revealing transformed steel micro-volumes between closely-spaced twin planes. (d) Twin boundaries (arrows) in the FIB thin foil. The STEM inset image shows that the twin boundaries continue beyond the termination of the LBE penetration (cross).

Figure 3. (a) STEM image of the area between two closely-spaced (0.6-0.8 μm) twin boundaries decorated by LBE (bright areas). (b-d) EDS elemental maps showing local Cr/Ni removal and Fe enrichment relative to the unaffected steel. (e) t-EBSD phase map showing a crystal structure change from *fcc* (austenitic matrix) to *bcc* (ferrite) between deformation twin boundaries. (f) EDS line scan across ferritized grains formed at twin boundary junctions shows Ni/Mn/Cr removal from the grain bulk and Pb/Bi presence at grain boundaries (arrows).

Figure 4. t-EBSD phase maps showing (a) a ferritized (*bcc*) micro-volume (Euler angles: 106.3, 33.2 and 86.2°) in an *fcc* steel matrix, and (b) twin (red, *fcc*) crystals oriented 60° relative to the steel matrix (blue, *fcc*). The Euler angles are 245.8, 17.0 and 29.5° for the twin crystal and 170.5, 50.9 and 44.3° for the steel matrix. Map acquisition with a step of 0.0206 μm. (c) Schematic representation of twin boundary-accelerated ferritization of austenitic stainless steels in LBE.

GRAPHICAL ABSTRACT