STUDY ON ENVIRONMENTALLY ASSISTED CRACKING OF STRUCTURAL MATERIAL FOR LFR REACTOR BY SSRT MECHANICAL TESTS

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Abstract

The development of Generation IV energy systems using heavy liquid metal (HLM) as a coolant is conditioned by the availability on the market of structural materials capable to operate under the conditions imposed by these systems. In the case of Lead cooled Fast Reactor (LFR), the operating conditions involve high temperature (450^0C - 550^0C) and long-term resistance of the material to a high flux neutron radiation. The objective of this work was the study the effect of the environmentally assisted cracking mechanism (EAC) of the 15-15Ti austenitic steel, a structural material used in the manufacture of fuel elements. From the analysis of the obtained results, a decrease in the tensile strength can be observed in the case of the samples tested in the lead environment under the same temperature conditions as in the air. This aspect is highlighted by fitting on the same graph the tensile curves obtained by tests in air and the liquid lead environment using MATLAB. The decrease in tensile strength is due to the interaction between the tested material and the liquid lead medium. SEM metallographic analyzes highlight the existence of a mixed fracture type in which both ductile fracture zones, characteristic of austenitic steel fracture and brittle fracture zones are present, which are the result of embrittlement due to the interaction between the material and the liquid lead environment. The evaluation of the EAC phenomenon is done by taking into account the effect of the corrosion mechanism combined with the plastic deformation. Thus, the corrosion mechanism causes the formation of an oxide layer on the surface of the material as a result of the interaction between it and liquid lead under temperature conditions. Scanning electron microscopy analysis revealed that this oxide layer was not uniform, ranging between 1.20 and 1.73 μm, and also had a porous appearance. The effect of plastic deformation was observed and highlighted on the SEM images in the form of microcracks mainly clustered towards the area of the fracture surface.

Keywords: *Generation IV, Heavy liquid metals, LFR reactor, EAC mechanism, SSRT*

Introduction

The qualification of structural materials operating in heavy liquid metals (HLM) is a key issue in the development of HLM-cooled nuclear reactors [1-3]. Potential degradation (in the absence of irradiation) includes general and local corrosion, environmentally assisted cracking (EAC), and embrittlement.

Embrittlement is generally considered as liquid metal atom penetration/diffusion into the base material, which affects the material mechanical behaviour. The phenomenon called liquid metal embrittlement (LME) is usually associated with the risk of premature unstable fracturing of components in contact with liquid metals.

Chronologically, for HLM structural materials, LME has been associated with the observation of the ductility "trough", i.e. the decrease in ductility of the tensile test specimen in contact with HLM, function of temperature and strain rate. Specifically, for T91 steel in lead is between 350°C and 425°C [4, 5], and for T91 in lead-bismuth eutectic (LBE) is between 160°C and 425°C. However, the presence of Pb/Bi atoms inside the material was not directly verified.

The ductility "trough" explanation has been ambiguous. The observed effect can be explained by both LME and EAC. It can be considered that more cleavage-like EAC cracks initiating from the surface being in contact with the HLM and their growth would also reduce the elongation of the specimen. Cleavage-like facets have been observed in many dedicated tests [6].

In addition, two facts supporting the idea of EAC have been recently demonstrated for T91 steel [1]. First, it was shown that the degradation disappeared if the surface was cleaned of liquid PbBi after 1000 hours of exposure at 500°C with low oxygen concentration [7]. Secondly, it was observed that the liquid metal atoms did not penetrate the material matrix, but only locally in the plastically deformed regions of the steel [8]. Based on recent studies, the degradation of structural materials in HLM, which has been attributed to LME, is better considered a special case of EAC, i.e., LME/EAC.

In the current understanding, the controlling factor of LME/EAC degradation is probably the adsorption of the liquid metal on a bare metal surface [9]. The key effects supporting this hypothesis are given in the following:

(i) the cracking sensitivity of the material decreases with temperature increasing, reaching the highest value above the melting point of the liquid metal (127°C for LBE, 328°C for Pb);
(ii) crack propagation is faster than the diffusion rate of heavy metal atoms;
(iii) wetting is the prerequisite for cracking [1, 10].

Compatibility of structural materials with liquid lead

Corrosion of liquid metals can have various effects on the operation of reactor systems.

Loss of material due to corrosion can affect the integrity of structural components. This issue is particularly important for thin-walled components, such as fuel elements and heat exchanger tubes. The liquid lead contains oxygen which causes a protective oxide deposit to form. The increased oxide layer on the metal surface can reduce heat transfer through the metal walls. This is important for components for which heat transfer is part of the operating process. As an example, it can mention the fuel element through which the heat produced by the nuclear reaction in the fuel is transferred to the coolant, and for the heat exchanger tubes through which the heat exchange takes place between the primary and the secondary circuits. Therefore, in addition to corrosion, the oxide layer thickness can be one of the criteria to define the lifetime of these components [11].

Dedicated experimental studies are conducted to evaluate these corrosion degradation effects. Different experimental data analysis approaches should also be applied to evaluate component performance. The evaluation of the fuel elements integrity should be based on the maximum corrosion penetration, while the evaluation of the heat exchanger performance is usually based on the average surface coverage by the oxide films and their thermal conductivity.

Various approaches to mitigate liquid metal corrosion (LMC) developed to date can be applied, as follows:

- selection of corrosion-resistant materials and definition of an appropriate range of coolant operating parameters, including temperature and dissolved oxygen concentration;
- doping of steels with elements that favour the formation of protective oxide layers, e.g. Si and Al;
- application of protective layers or surface alloys;
- addition of inhibitors to the coolant, e.g. Zr.

Oxygen concentration in liquid lead alloys is a key parameter for the structural materials corrosion. For oxygen concentrations in the range 10^{-8}%wt - 10^{-10} %wt, dissolution corrosion occurs, while for concentrations greater than 10^{-7}%wt, oxidation of steels occurs (Fig. 1).

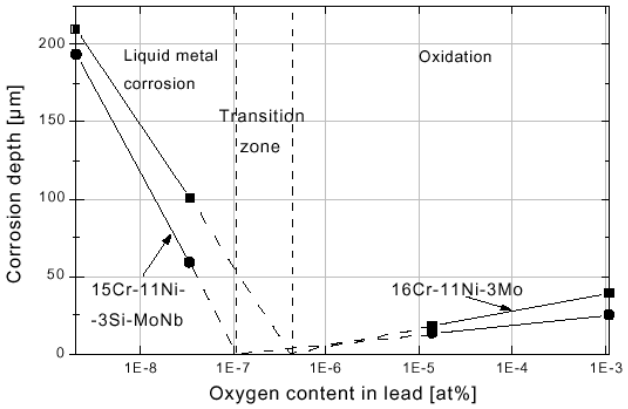


Fig.1. Dissolution/oxidation depth of stainless steels in lead at 550°C for different oxygen concentrations in the liquid metal

The liquid lead environment effect on the mechanical properties of austenitic steels

The use of liquid heavy metals (HLM) and especially lead-bismuth eutectic (LBE) or lead for Generation IV liquid metal-cooled nuclear systems requires an assessment of their compatibility with the structural materials. Their development requires that the material compatibility problem be solved, with and without irradiation, either under the mixed proton-neutron spectrum typical for the spallation source of an accelerator driven system (ADS) or under the fast neutron spectrum typical for a fast reactor.

The mechanisms of mechanical properties degradation through interaction with liquid metals can be classified as follows:

- Liquid metal embrittlement (LME),
- Liquid metal-assisted damage (LMAD)
- Environmentally assisted cracking (EAC).

Liquid metal embrittlement – LME

LME represents the loss of ductility of a normally ductile metal or metal alloy when stressed in contact with a liquid metal that can lead to brittle fracture. LME is considered a particular type of brittle fracture, intergranular (IG) or transgranular (TG), by cleavage occurring in the absence of an inert medium and at low temperatures. In other words, a time- and temperature-dependent fracture process will not be considered a manifestation of LME.

LME failure occurs through the nucleation of a crack at the wet surface of a solid and its subsequent propagation into the material matrix until rupture. The prerequisites for LME are listed below:

- Intimate or direct atomic-scale contact between solid and liquid metal phases is a concept classically interpreted as wetting.
- Stress is applied at a level sufficient to produce plastic deformation, even though the required deformation can be produced, on a microscopic scale, at stresses well below the engineering yield strength.
- Existence of stress concentrators or pre-existing obstacles to the movement of dislocations. This requirement is found in the literature, but it is not considered as important as the two criteria previously mentioned.

A widely accepted explanation of LME failure is based on the Griffith criterion that establishes the fracture stress σ_F for crack propagation [12], modified to take into account the Rebinder effect, i.e. the reduction of the surface free energy, γ_{sl}, by the adsorption of a liquid metal relative with an inert medium [13]. Σ_F is written like this:

$$\sigma_F = \sqrt{\frac{E\gamma_{sl}}{2c}} \tag{1}$$

where E is Young's modulus and c is the crack size or its radius in the case of an internal defect, as shown in Fig. 2 [12]. Eq. (1) assumes that the change in stored elastic strain energy is entirely used in the fracture process to create new fracture surfaces.

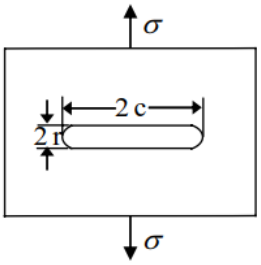


Fig. 2. A flat crack of length *2c* and width *2r* in a plate subjected to tensile stress σ perpendicular to the length of the crack

In real situations, rupture does not occur as a result of the development of an elastic microcrack, because a crack cannot be stable in an ideal network; as soon as it appears, it will develop at a speed of about the speed of sound throughout the crystal, if there is no barrier to its development. In real situations, Rebinder and Shchukin [14] proposed to include the plastic deformation of the material accompanying crack growth and to write critical fracture stress as:

$$\sigma_c = \mu\left(\frac{E}{c}\right)^{1/2}\left(\gamma_p + \gamma_{sl}\right)^{1/2} \tag{2}$$

where μ, E, γ_p and γ_{sl} are a proportionality coefficient, Young's modulus, contribution to plastic deformation, and free energy at the solid-liquid interface, respectively.

Liquid metal-assisted damage – LMAD

Unlike LME, LMAD refers to a liquid metal effect that accelerates fracture without any change in the fracture mode. No corrosive effect occurs during LMAD. The prerequisites for LMAD are the same as those listed above for LME.

Environmentally assisted cracking – EAC

Environmentally assisted cracking refers to the premature and catastrophic failure of a material in the simultaneous presence of tensile stress and a mildly corrosive environment.

The prerequisites for EAC are as follows:

- Liquid metal-induced corrosion (LMC), which can be localized, intergranular, or uniform or, on the contrary, which can lead to the growth of an oxide film on the surface of the solid metal, is considered a main requirement for the occurrence of EAC. As indicated above, LM corrosivity can be very limited, affecting only the superficial solid layers.
- Plastic deformation, interacting with corrosion, characterizes EAC at all stages of the process.

Just to remember that corrosion and consequently, EAC is time dependent. Therefore, a liquid metal-induced degradation of mechanical properties that will be a function of aging time in LM will be considered a case of EAC. Also, the crack growth rate in EAC never reaches the values reported in LME, which can reach 10^{-1} m/s for some brittle couples [15].

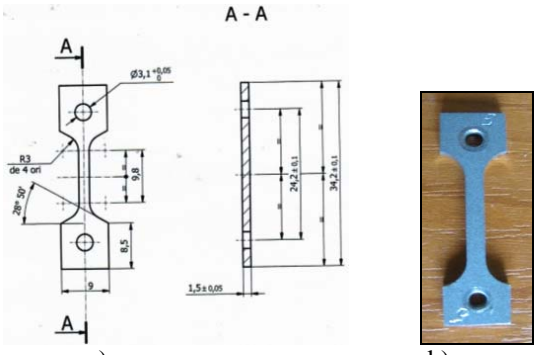
The mechanical test to highlight the EAC effect

As defined and presented in the literature, the environment-assisted cracking phenomenon implies the existence of mechanical stress in the nuclear reactor component and the presence of a corrosive medium, which in our case is liquid lead.

To highlight this phenomenon, SSRT (Slow Strain Rate Test) mechanical tests were carried out. They allow the liquid lead to penetrate the spaces created by the production and growth of cracks in the material [16].

The specimens used (tube and sheet) were made of austenitic steel type 15-15Ti. The plates taken from the sheet were made according to the American ASTM E8 standard, with a thickness of 1.5 mm, of about 34 mm in length, and a calibrated area with a length of 9.8 mm.

Fig. 3 shows the sketch and layout of the tested samples. Currently, austenitic steel 15-15Ti (15%Cr-15Ni-1.6Mn-1.5Mo-0.8Si-0.4Ti) is considered an alternative fuel cladding material, mainly because the steel should not be susceptible to LME. However, 15-15Ti would have several times more swelling when irradiated at high doses compared to the ferritic-martensitic steels.



a) b)

Fig. 3. Flat tensile test specimen: a) sketch, b) shape

The mechanical tests were carried out with the Instron machine on which an electric furnace dedicated to tests in the liquid lead environment was adapted (see Fig.4). The traverse speed was v_T = 0.03 mm/min, which corresponds to a deformation speed $\dot{\varepsilon} = 5 \cdot 10^{-5}\, s^{-1}$.



Fig. 4. Experimental Set-up

The test temperature was 400 °C. From the obtained results analysis, a decrease in the tensile strength can be observed in the case of the samples tested in the lead environment under the same temperature conditions as in the air. This aspect is highlighted by superimposing on the same graph the tensile curves obtained by the tests in air and the liquid lead environment using MATLAB (Fig. 5). The decreasing in tensile strength is due to the interaction between the tested material and the liquid lead medium.

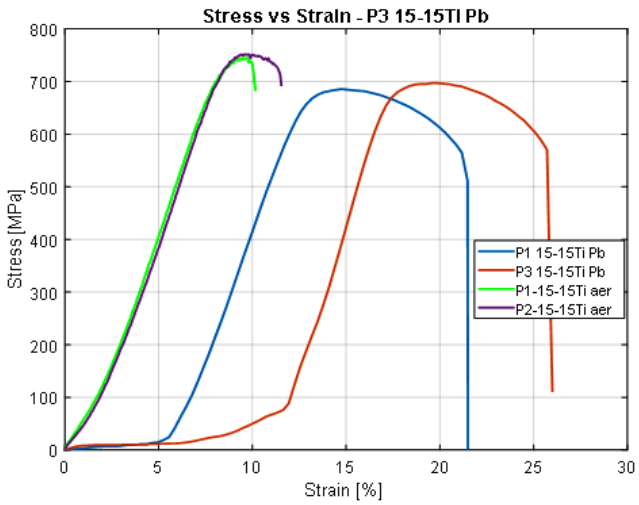


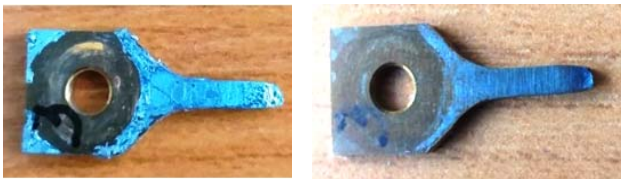
Fig. 5. Stress-strain curves
(comparison between liquid lead medium and air)

The decrease is not significant, being somewhere around 7-8%. One of the reasons may be the short retention time of the specimens in the liquid lead medium. Summing the time of introducing the specimen into the pre-heated lead, the time of closing the furnace and instrumentation, the holding time in the bearing and the actual mechanical testing time of the specimen, will result a total holding time of the specimen in the lead environment of about 4 – 5 hours (valid for tests at 400°C).

Microstructural analyses

The microstructural analyzes aimed to clarify aspects related to the influence of the liquid lead environment on the material properties of the 15-15Ti austenitic steel. As part of the work, scanning electron microscopy (SEM) analyzes were carried out.

The samples subjected to testing were both clean and unclean of the residual lead deposited during the test. Cleaning was done with a solution consisting of 4ml H_2O_2 and 2ml CH_3COOH. The cleaning process was carried out at room temperature. In the first phase, the sample was kept in the solution for 180 seconds. After wiping, the need for a new immersion in the solution was found. The second hold phase was also for 180 seconds. Fig. 6 shows the appearance of the sample before and after cleaning.



a) b)

Fig. 6. 15-15Ti austenitic steel specimen:
a) before cleaning, b) after cleaning

Fig. 7 shows an image of the fracture surface, somewhere in the central area to highlight the very good cleaning of the residual lead. A small spot of lead can be seen on the image, the rest of the surface is clean.

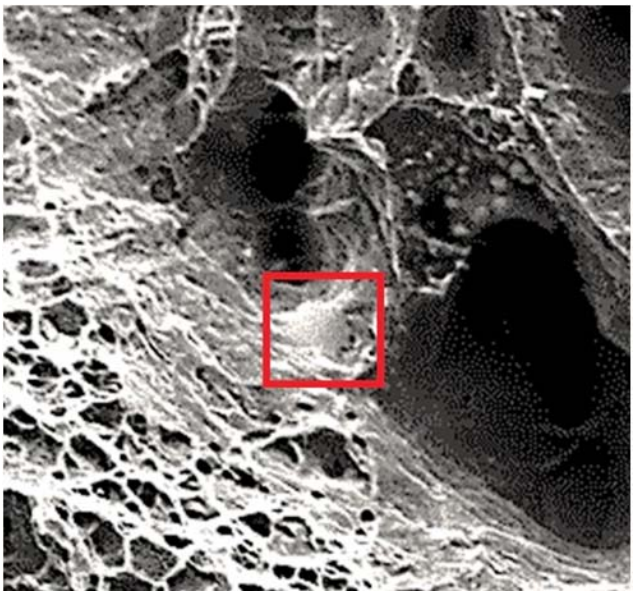


Fig. 7. The fracture surface of 15-15Ti austenitic steel specimen (residual lead trace highlighted)

The SEM analyzes were carried out with the Tescan Vega LMU microscope using the secondary electron detector.

A first analysis was made on the fracture surface of the specimen from Fig. 6b) and the obtained images are presented in Fig. 8.

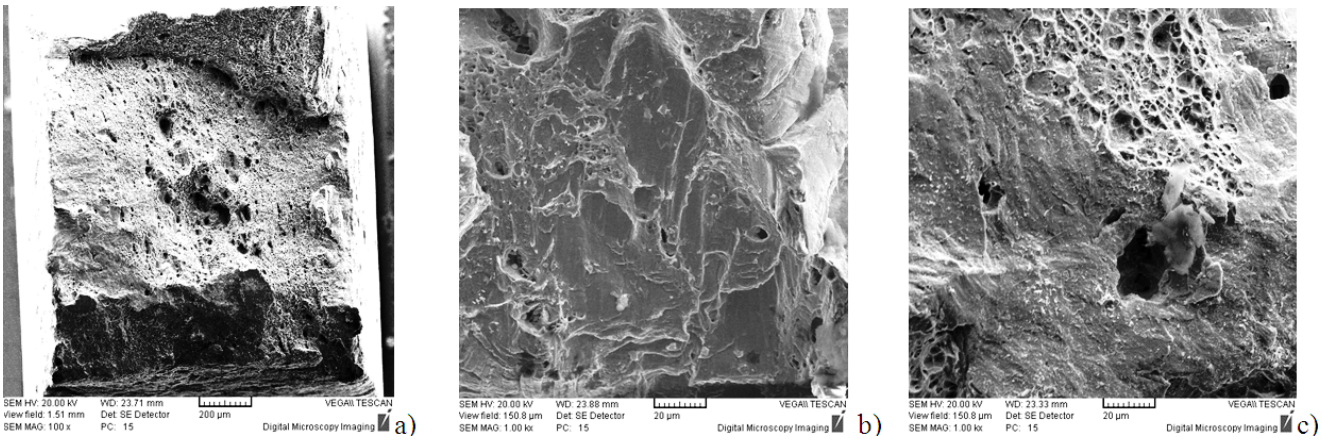


Fig. 8. 15-15Ti austenitic steel specimen fracture surface:
a) total fracture surface, b) and c) details of different areas of the fracture surface

The SEM aspects shown in Fig. 8a) comprise an overview of the entire fracture surface at x100 magnification. Then details of different areas of the fracture surface are presented. The image in Fig. 8b) is acquired in the centre of the rupture area, the image presented in Fig. 8c) being acquired in the edge area. Analyzing these images, it can be noticed a mixed fracture type in which there are both areas with ductile fracture, characteristic of the fracture of austenitic steel 15-15Ti, and areas with brittle fracture which we consider to be the result of embrittlement due to the interaction between the material and the lead environment liquid. This observation is supported by the experimental data obtained by the tensile test where the decrease of the tensile strength was found in the case of the specimens tested in the liquid lead.
The EAC is governed by two simultaneously occurring phenomena: corrosion induced by liquid metals and plastic deformation. Using SEM microscopy, both phenomena were highlighted. Corrosion can be localized, intergranular, or uniform, or, on the contrary, it can lead to the growth of an oxide film on the solid metal surface. To be able to visualize the oxide layer produced on the sample surface, the backscattered electron detector was used.

Fig. 9 shows the tensile specimen on which the oxide layer was formed. To observe the difference between the images acquired with the backscattered electron detector and the images acquired with the secondary electron detector, the same area investigated with both detectors is shown.

Considering the relatively short test time, it is observed that the oxide layer is uneven and porous, exfoliating easily during sample preparation. The uneven aspect is also highlighted in Fig. 10 where, by measuring several points, different thicknesses of the oxide layer were obtained. The variations of the oxide layer deposited on the surface of the 15-15Ti austenitic steel are between 1.20 µm and 1.73 µm.

Plastic deformation interacts with corrosion and results in the appearance of microcracks on the specimen surface. SEM investigations were performed on the specimen entire facet (Fig. 11), but the microcracks were predominantly found in the area toward the fracture surface.

Fig.12 shows SEM images with microcracks found on the investigated surface.

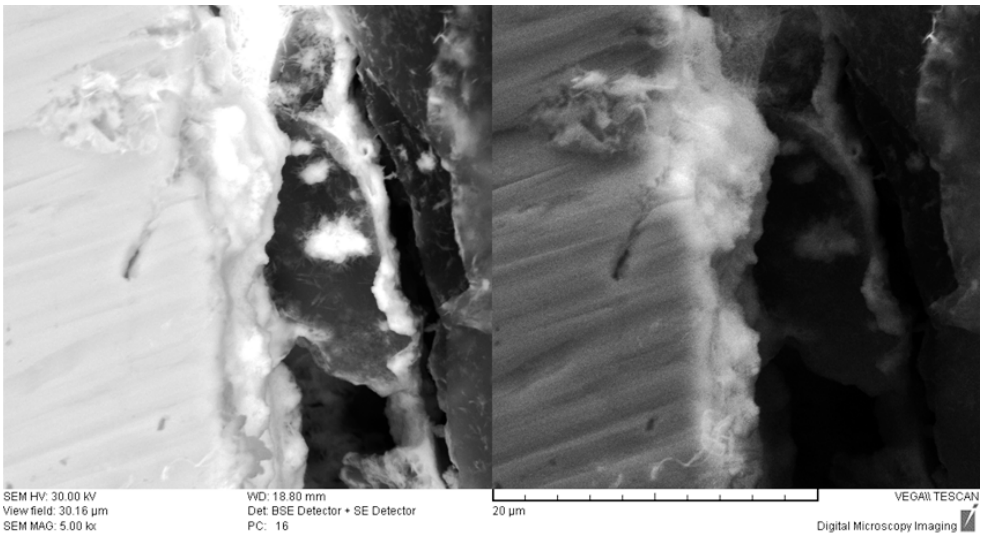


Fig. 9. SEM images on the chemically cleaned surface of the 15-15Ti austenitic steel specimen:
a) backscattered electron image, and b) secondary electron image

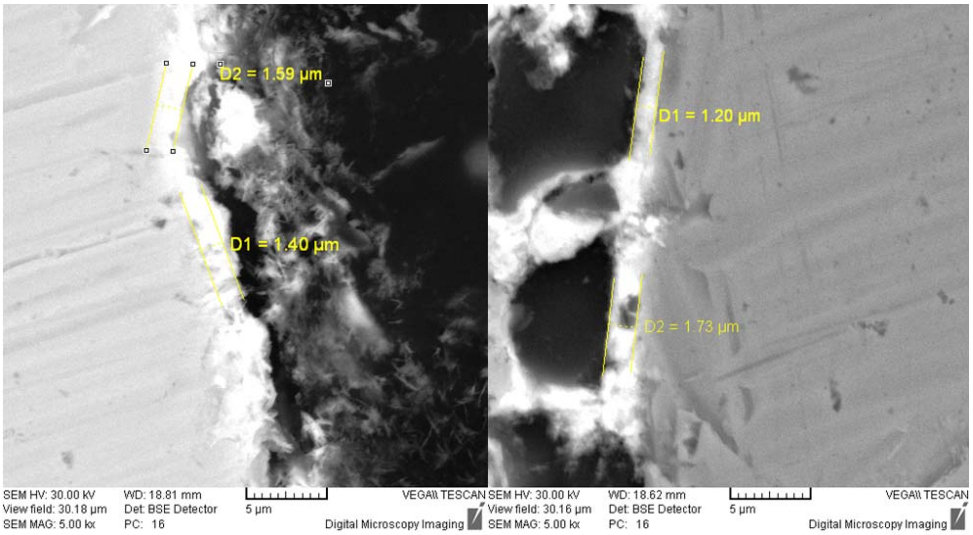


Fig. 10. Measurements of the oxide layer in several areas of the specimen

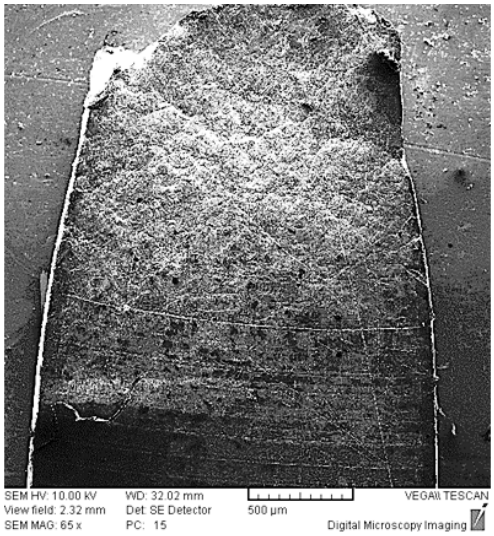


Fig. 11. The surface of the specimen investigated for microcracks

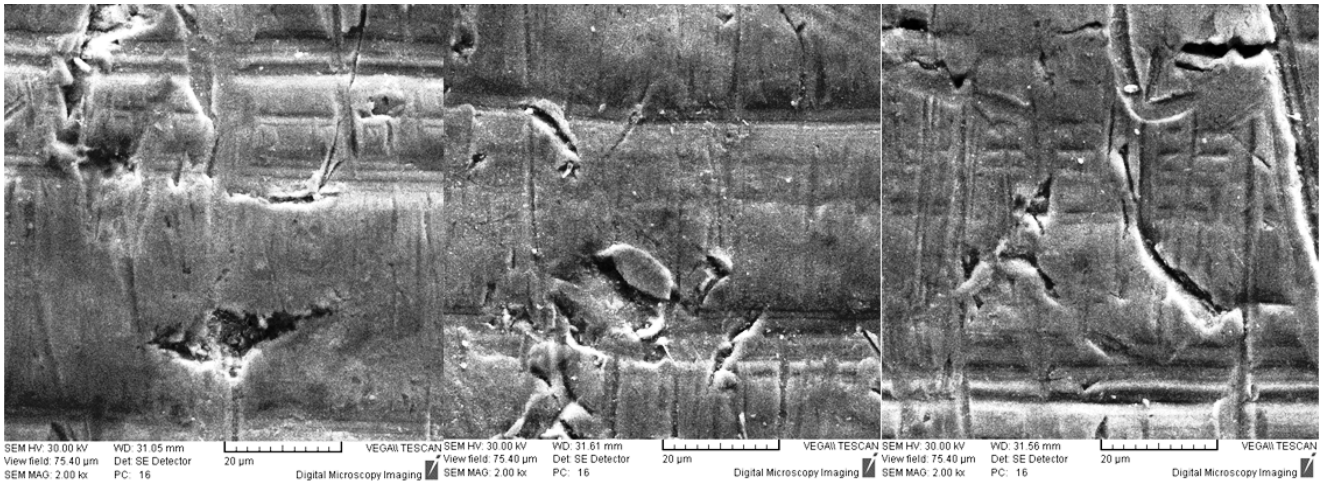


Fig. 12. Microcracks on the surface of the 15-15Ti austenitic steel specimen

Conclusions

The present work objective was to carry out a study on the phenomenon of cracking assisted by the liquid lead medium known in the literature as "environmentally assisted cracking - EAC". The aim was to highlight the influence the liquid lead has on the mechanical properties of the candidate materials for the LFR reactor.

In the first step, it was emphasized that good compatibility between the structural materials and the liquid lead environment is conditioned by the knowledge of the degradation mechanisms induced by the dissolution of oxygen in the lead and the monitoring and regulation of this oxygen content in the liquid lead environment. The main degradation mechanisms were presented with emphasis on the EAC mechanism.

The test matrix for highlighting the influence of the lead environment on the material properties included performing of SSRT tests on 15-15Ti austenitic steel samples in the liquid lead environment, in a static regime at a temperature of 400°C. The SSRT type test was used as the test method because it takes place at very low mechanical stress application speeds which allows the liquid lead to penetrate the spaces created by the production and growth of cracks in the material.

From the analysis of the obtained experimental data, the effect of the lead environment on the mechanical properties of the 15-15Ti steel was highlighted. Thus, the tensile strength decreases in the case of the samples tested in the lead environment compared to the samples tested in air, at the same temperature of 400°C. This decreasing appears as an effect of the interaction between the tested material and the liquid lead, an interaction causing embrittlement of the steel. The decrease is not significant, being somewhere around 7-8%.

The microstructural analysis performed complements the experimental results. The effect of the lead environment on the material is also highlighted by the analyzes made on the fracture surface where a mixed type of fracture is observed. Both areas are visible: area with ductile fracture, characteristic for austenitic steel 316L, and area with brittle fracture, considered the result of embrittlement due to the interaction between the material and the liquid lead environment.

The oxide layer, observed by SEM investigations, is also an effect of the liquid lead-material interaction as corrosion leads to the growth of an oxide film on the metal surface.

In the future, the research activities proposed will continue the experiments on samples in the liquid lead considering longer exposure times, and also with the study of the effect of repeated solidification of the cooling agent on the mechanical properties of the Gen IV structural materials.

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