

Microstructural and mechanical properties of Al-base coated EUROFER-97

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ABSTRACT

Coolant-facing alloys in a tokamak will face harsh environments due to the synergistic effect of flowing coolant, dynamic mechanical loading, ionising radiation, and tritium embrittlement. Reduced activation ferritic/martensitic (RAF/M) EUROFER-97 is the primary candidate as the structural alloy for the breeder blanket to be used in DEMO reactor. Under fusion-like conditions, coatings are required to improve both its corrosion properties and act as a tritium permeation barrier (TPB) layer. In this study, Al-base self-passivating coatings have been investigated as possible solution to provide protection against corrosion and act as TPB layer. The aim of this study was to assess the adhesion properties between different self-passivating Al-base coatings as electroplated and chemical vapour deposited (CVD) coatings on a RAF/M EUROFER-97 under strain. These studies showed the high ductility of pure electroplated Al-coatings, whereas both CVD coatings cracked under the applied strain.

1. Introduction

EUROFER-97 is a reduced activation ferritic/martensitic (RAF/M) steel developed for structural applications in the European ITER (International Thermonuclear Experimental Reactor) and DEMO (DEMONstration Power Plant) fusion reactors [1–6]. The particular chemical composition of this alloy has been developed to reduce the long-lived radionuclides that can be produced by the expected fusion neutron spectrum [7] and due to the increase in ductile to brittle transition temperature under neutron irradiation [8,9]. Specifically, EUROFER-97 has been designed to be the structural alloy for the breeder blanket section, and therefore it may be either exposed to high temperature water, used as coolant at $\approx 300^\circ\text{C}$, or to the breeder liquid PbLi at $\approx 550^\circ\text{C}$ [10–12].

To both improve the corrosion properties and to minimize the permeation of tritium under both environments, oxide coatings have been proposed as a possible mitigation strategy. Erbium (Er_2O_3) and Yttria (Y_2O_3) are the most stable oxide coatings under liquid PbLi, however, their availability and the cost for large scale application can limit their use [13]. Moreover, prolonged exposure times can still partially dissolve the surface oxide, and the formation of cracks in the coatings due to vibration of the plant can still expose the underneath material to the coolant environment, thus locally enhancing oxidation and tritium permeation. Therefore, Al-base coatings have been proposed as one candidate coating [13–15] for enhanced corrosion protection and as

tritium barrier layer. Under high temperature aqueous conditions, Al can form a stable and protective Al_2O_3 [13,14] layer, and in the case of local cracking, the underneath Al can interact with the environment during service thus creating a new protective oxide layer, thus self-healing (*i.e.*, self-passivating) the coating itself during the operating lifetime of the plant [13,14,16–19]. For example, alumina-forming austenitic (AFA) steels [19] are considered a promising candidate in high temperature corrosive environments, with studies showing higher resistance to corrosion compared to commercial austenitic steels [16–18]. In fact, alumina scale is more stable than the Cr-rich oxide scale [20] and it can also alleviate the chromium volatilization in between 800°C and 900°C in air with 10 % H_2O [20]. Moreover, Al-base coatings can be used to protect the structural alloys that are designed as coolant/breeder facing alloys, for applications that use liquid PbLi as breeder [10–12]. Under Li-rich liquid environments, possibility of doping the liquid metals with nitrogen (N) could promote the formation of a stable aluminium nitrides (AlN) layer that would be stable under pure Li environments [21], however further studies are still needed.

Several studies have been reported in literature on the use of Al-base coating to improve corrosion and limit the diffusion of tritium in EUROFER-97 [22–28], however, there are no studies on TPB layers tested under stress/strain and therefore further studies are needed in order to assess the effective use of Al-base coatings as possible barrier layer against both aqueous coolant and liquid metal breeder environments for fusion applications. In this study, EUROFER-97 coated with

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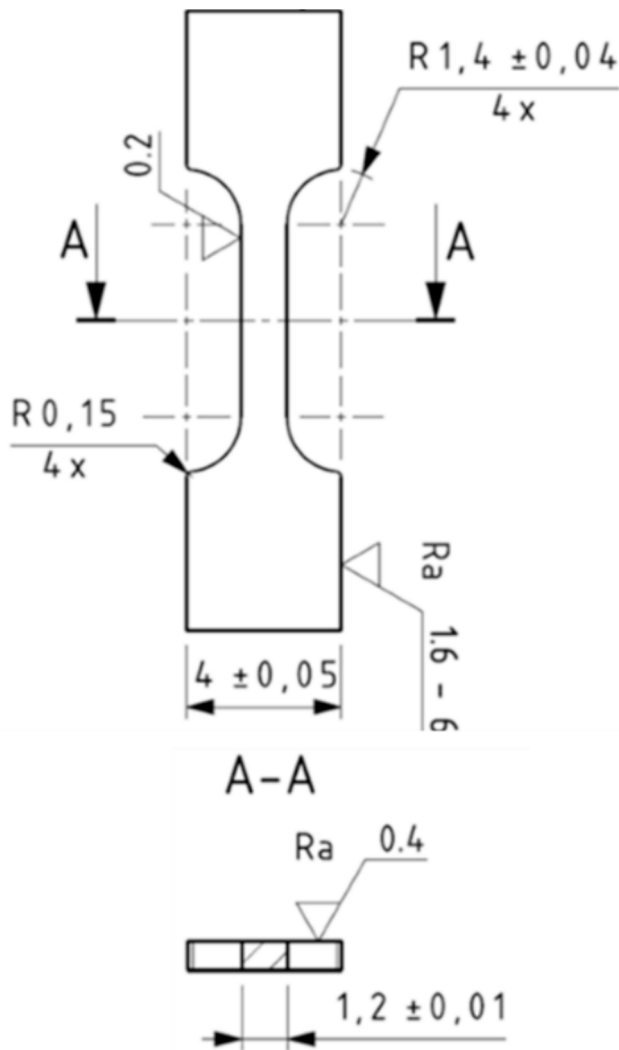


Fig. 1. Schematic of the EUROFER-97 SS-J3 type geometry, where the dimensions are in mm.

Al-base coatings have been studied to investigate the adhesion properties of an electroplated and two chemical vapour deposition (CVD) [29–31] Al-base coatings under strain. CVD processes have already been proposed as TPB for fusion application, and therefore further investigated in this study, however the high temperature used for the coating process may detrimentally modify the near surface region of the EUROFER-97. The Al-base electroplating technique was investigated as possible alternative to the high temperature CVD processes in order to retain the original near surface region of EUROFER-97 and understand how this could impact on TPB and anti-corrosion properties. The coated EUROFER-97 specimens were strained up to $\approx 1\%$ engineering straining, and microstructural analysis techniques were used to assess any failure or delamination between the Al-base coatings and the EUROFER-97.

2. Experimental procedures

2.1. Material and specimen preparation

2.1.1. Material

In this study, SS-J3 type dog bone specimens (Fig. 1) with a thickness of 0.75 mm, a total length of 16 mm and a gauge length of 5 mm were used as coupon specimens to study the response under strain and adhesion properties of the Al-base coatings on the RAF/M EUROFER-97.

The specimens were extracted from a EUROFER-97 plate (Heat no. 993394, batch 3) provided by EUROfusion. The EUROFER-97 plate was manufactured by Saarshiede Freiformschmiede GmbH and hot rolled by • Bohler Bleche GmbH & Co. The plate was normalized at 980 °C for 10.8 min and cooled in air, then tempered at 760 °C for 90 min and then finally cooled in air. The chemical composition of the plate is shown in Table 1.

Both surfaces of the specimens were metallographically polished to obtain a mirror finish surface with a 1 μ m diamond solution. The specimens were coated with either one of the following processes: electroplating AlumiPlate®, chemical vapour deposition (CVD) Batch 1 (CVD1) or CVD Batch 2 (CVD2). The electroplated specimens were plated at room temperature with a minimum thickness of 10 μ m of high purity (99.99 wt%) aluminium by AlumiPlate Inc. (US). The CVD processes were performed by Diffusion Alloys (UK) Ltd. The specimens were placed into pots with a powder mixture formed by Al, Cr, Al₂O₃ and NH₄Cl and kept under a slightly reducing environment formed with a 95 %Ar-5 %H₂ gaseous mixture. At the end of the coating run, the pots were furnace cooled. The specimens coated with the CVD1 process were exposed at the temperature of 700 °C, whereas the specimens coated with the CVD2 at 750 °C.

2.1.2. Baseline material characterization

After the Al-base coatings process, representative SS-J3 specimens were cross-sectioned with a high-speed cutting machine, mounted in Bakelite and metallographically polished with grinding papers and diamond solution of 3 μ m and 1 μ m. The specimens were rinsed with soapy water between each step to avoid contamination. The last polishing step was performed by using a 24–40 nm SiO₄ oxide polishing suspension (OPS). This step was necessary to remove any deformation induced by the previous grinding steps and to obtain a stress-free surface representative of the bulk material. The specimens were finally cleaned with soapy water, rinsed with deionised water to remove any residue of OPS, and then dried in a stream of hot air.

2.2. Straining

The SS-J3 type specimens were tested in an Instron Machine 5966 with a 10 kN head. The specimens were strained in air at room temperature until a 1 % nominal strain was reached at the rate of $1 \times 10^{-3} \text{ s}^{-1}$. An alignment cartridge was design to remove potential torsion during the straining phase. The 1 % straining was monitored using digital image correlation (DIC) by monitoring a speckle particle pattern. A Fengda® AS-186 compressor and an airbrush spray gun were used to apply an even coating of black acrylic spray paint onto the surface of interest. This creates a black base on which a contrasting white speckle pattern is visible. The speckle pattern was created with white acrylic spray paint and sprayed by setting the compressor pressure at 40 psi. The specimen was checked and monitored during straining with the software

Table 1

Chemical composition (wt. %) for the substrate EUROFER-97 used in this study and provided by EUROfusion.

C	Si	Mn	P	S	Ni	Cr	Mo	V
0.105	0.024	0.56	0.0025	0.001	0.013	9.08	0.005	0.235
W	Ti	Cu	Nb	Al	N ₂	Ta	Co	Fe
1.07	0.001	0.005	0.005	0.009	0.039	0.125	0.007	Bal.

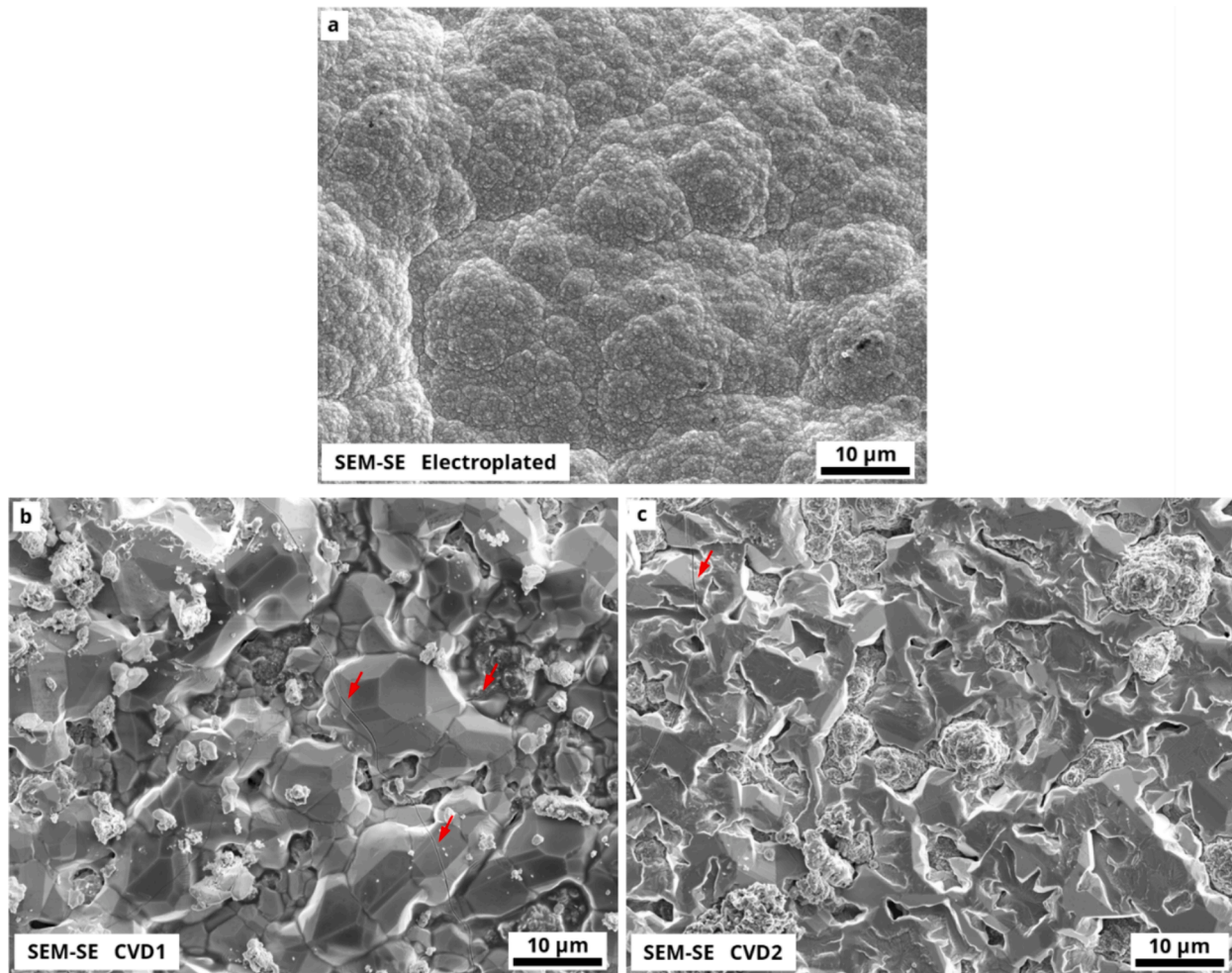


Fig. 2. SE SEM top surface micrographs of the baseline EUROFER-97 with (a) electroplated, (b) CVD1 and (c) CVD2 Al-base layer. The micrographs showed the presence of randomly distributed cracks (red arrows) for both CVD1 and CVD2 coatings.

LaVision DaVis ver. 10.2.1. After the tensile test, the specimens were rinsed with acetone to remove any residue of the dark coating and bright speckle pattern.

2.3. Material characterization

2.3.1. Microscopy characterization

The specimens were analysed with a number of different microstructural techniques. A field emission gun (FEG) scanning electron microscope (SEM) TESCAN MIRA equipped with an Oxford Instruments (OI) silicon drift detector (SDD) X-Max 80 and an OI electron backscatter diffraction (EBSD) detector Symmetry S2. The FEG-SEM was used to perform initial assessment of the surface and cross sections of the specimens before and after straining. The microstructure of the near surface region was identified via EBSD. EBSD maps were acquired with an electron voltage of 20 kV, with a nominal current of 600 pA, a working distance of 20 mm on a pre-tilted specimen holder of 70°. The EBSD maps were acquired with a step size of 100 nm. Higher magnification EBSD maps were acquired for the specimens after straining and focussed on the interface EUROFER-97-Al base coatings (step size = 70 nm). The phase, inverse pole figure (IPF)-Y and grain reference orientation deviation (GROD) angle maps were obtained with the software OI

AZtec version 6.0 and analysed with AZtecCrystal version 2.2. The near surface chemical composition was obtained by performing SEM – energy dispersive X-ray (EDX) analysis. SEM-EDX point / “spot” analyses were performed at 15 kV with a real time of 60 s and a process time of 5 s. Elemental maps were acquired with a live time of 15 min and a process time of 5 s. The data were background subtracted and acquired with the software OI AZtec version 5.2, then analysed and processed with the version 6.0. The SEM-EDX point profile plots were obtained by using the Python libraries Pandas [32,33] and Matplotlib [34]. The thickness of the Al-base coatings was manually measured using ImageJ Fiji software with more than 50 data points collected for each Al-base coating process [35]. A dual beam FEG-SEM focussed ion beam (FIB) FEI Helios600 Nanolab was used to obtain detailed images of the microstructure in the near surface region before and after the straining test with the circular backscattered electron (BSE) detector with an accelerating voltage of 5 kV and a nominal current of 1.4 nA. Complementary grazing angle X-ray diffraction (GA-XRD) were used to identify the near surface crystal structure. The specimens were analysed with a Rigaku SmartLab X-Ray Diffractometer equipped with a Cu K α source with a 2 θ with a 0.1° step size. The XRD grazing angle was of 6° to limit the interaction of the beam with the substrate EUROFER-97. The Al₂O₃, FeAl₆, FeAl₃, Fe₂Al₅ FeAl and FeAl_{2.8} peak profiles were obtained from [36–41].

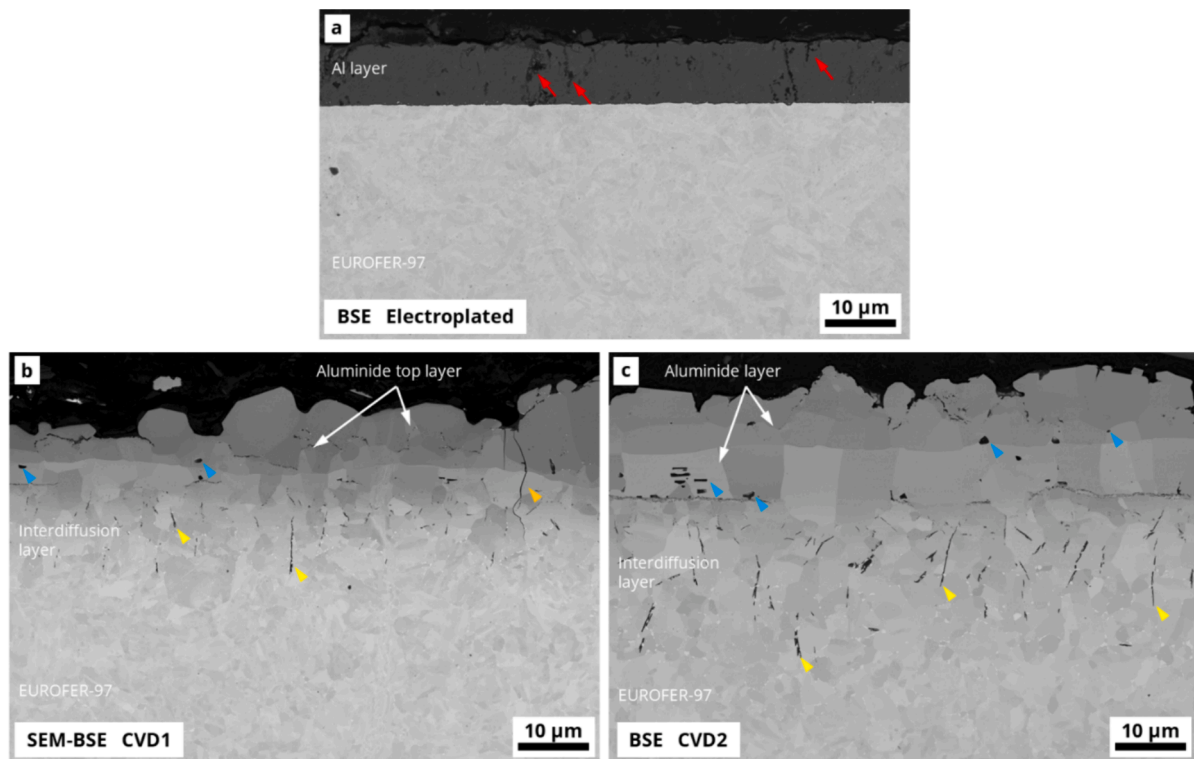


Fig. 3. BSE SEM cross sections micrographs showing the baseline near surface microstructure of the EUROFER-97 after (a) electroplated, (b) CVD1 and (c) CVD2 processes. The micrographs showed the deposition of the (a) electroplated Al-layer and the strong interaction between Al and Fe for both (b) CVD1 and (c) CVD2 processes.

Table 2

Summary of the thicknesses of the aluminised layers associated with the CVD1 and CVD2.

Al-layer	CVD1	CVD2
Aluminised top layer, μm	11.9 ± 3.4	15.6 ± 2.8
Interdiffusion bottom layer, μm	14.9 ± 2.7	31.2 ± 3.1

2.3.2. Nano hardness characterization

Nanoindentation was performed on sample cross-sections using a KLA iMicro nanoindenter. The area function for the Berkovich tip was calibrated using a fused silica reference sample, and the data were analysed using the standard Oliver and Pharr method [42]. Indents of 1 μm depth were performed using the continuous stiffness measurement (CSM) technique in targeted regions from optical contrast. All indents were spaced at least 20 times their depth from each other to avoid the plastic zone created by the previous indent. The summary values of hardness and modulus were obtained at a depth of 250 nm. This depth was chosen to avoid near surface effects but still maintain local measurement of the target region.

3. Results

3.1. Baseline material characterization

The top view surface of the three Al-base coated EUROFER-97 specimens is shown in Fig. 2. The surface of the electroplated EUROFER-97 specimen showed a globular microstructure (Fig. 2a),

whereas both CVD1 (Fig. 2b) and CVD2 (Fig. 2c) EUROFER-97 surfaces presented a highly corrugated surface, decorated with crystallites and globular features. Randomly distributed cracks were also noticed, indicated by red arrows in Fig. 2b and c.

Representative cross-sectional BSE images of the EUROFER-97 with either of the three Al-base coatings are showed in Fig. 3. The electroplated Al coating (Fig. 3a) showed good adhesion with a uniform thickness of $8.9 \pm 0.4 \mu\text{m}$. Faceted cavities, shown as darker regions in the coatings (red arrows in Fig. 3a) were identified in the Al-layer, however it is not possible to assess if these cavities are associated with the coating itself or with the polishing process.

The aluminised CVD1 (Fig. 3b) and CVD2 (Fig. 3c) processes produced a rough surface profile. The CVD coatings presented a double structure with an external aluminised layer and an interdiffusion layer. The summary of the thicknesses of each layer is reported in Table 2. Specifically, the higher temperature associated with the CVD2 induced a deeper interdiffusion layer, however the thickness of the external layers was comparable between CVD1 and CVD2 processes. The near surface region for both processes was decorated with elongated darkly imaging features (yellow arrows in Fig. 3b, c), cavities (light blues arrows in Fig. 3b,c) and cracks (orange arrows in Fig. 3b), where these latter features were possibly induced by the furnace cooling process.

Elemental SEM-EDX maps associated with the CVD1 process (Fig. 4) showed a that the aluminised coating was enriched in both Fe (Fe-K α) and Al (Al-L α), with Al diffused into the near surface region of the EUROFER-97 matrix for $\approx 20 \mu\text{m}$ (Al-L α in Fig. 4). Complementary semi-quantitative SEM-EDX point / “spot” analyses (plot c in Fig. 4) confirmed the chemical re-distribution in the near surface region of Al, Fe and Cr as shown in the secondary electron (SE) image in Fig. 4b. In

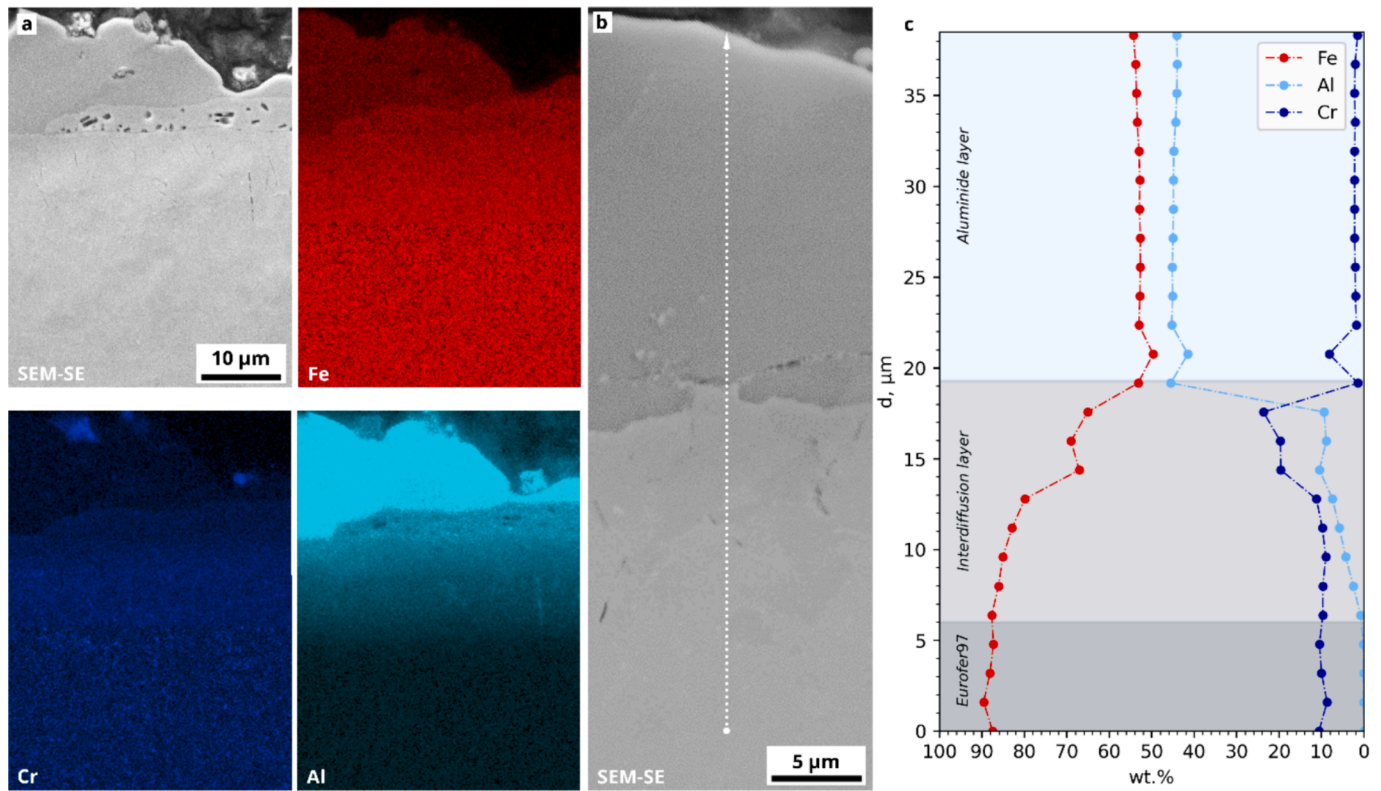


Fig. 4. (a) SE SEM micrograph and corresponding EDX elemental maps for Fe, Cr and Al for the CVD1 EUROFER-97 specimen. Note the strong presence of Al in the aluminised top layer and the diffusion within the EUROFER-97 matrix. (b) SE SEM micrograph and corresponding (c) semi-quantitative near surface region elemental distribution of Fe, Cr and Al for the CVD1 process, extracted from the white dotted line in (b).

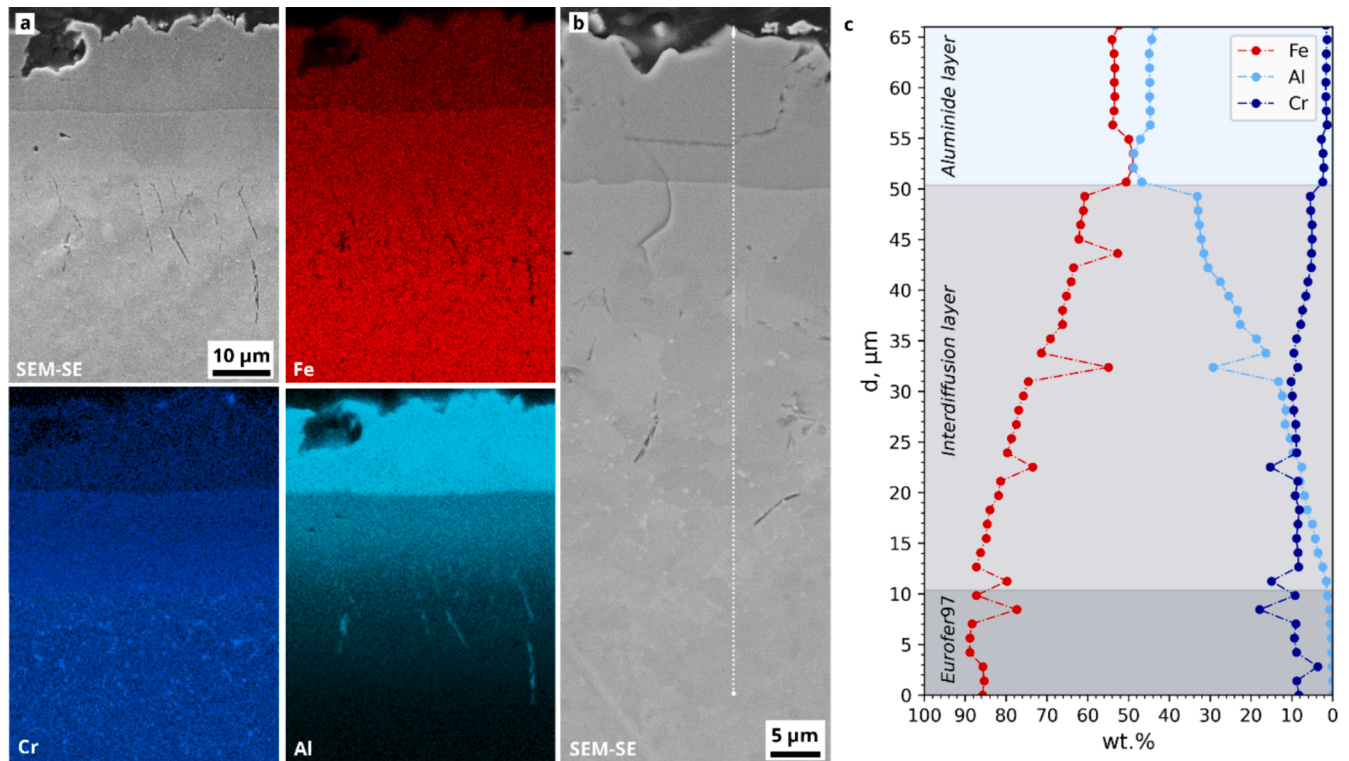


Fig. 5. (a) SE SEM micrograph and corresponding EDX elemental maps for Fe, Cr and Al for the CVD2 EUROFER-97 specimen. Note the strong presence of Al in the aluminised top layer and the diffusion within the EUROFER-97 matrix. (b) SE SEM micrograph and corresponding (c) semi-quantitative near surface region elemental distribution of Fe, Cr and Al for the CVD1 process, extracted from the white dotted line in (b). Note the presence of spikes in the Cr and Al chemical profiles, associated with local second phases present in the EUROFER-97 matrix.

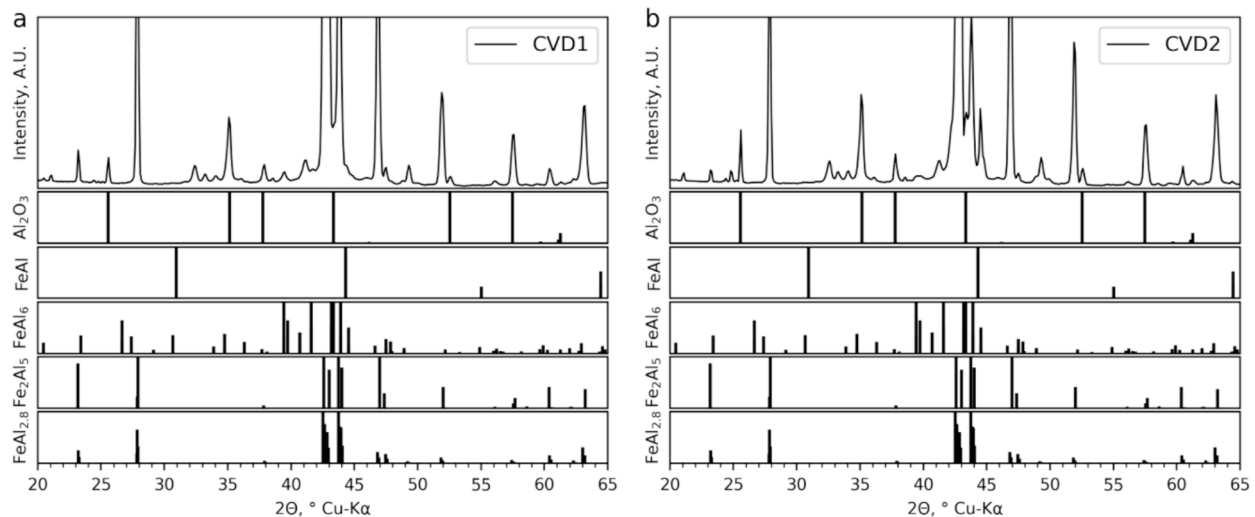


Fig. 6. (a) GA XRD spectrum for the (a) CVD1 and (b) CVD2 Al-base coatings. The experimental spectra were compared with the peak profiles of Al_2O_3 , FeAl, FeAl₆, Fe₂Al₅ and FeAl_{2.8} [37–41].

fact, the substrate EUROFER-97 was mainly composed by Fe ($\approx 85\text{--}90\text{ wt}\%$) and Cr ($\approx 9\text{--}10\text{ wt}\%$). Whereas, in the interdiffusion layer (from $\approx 6\text{ }\mu\text{m}$ to $\approx 19\text{ }\mu\text{m}$), the Fe dropped to $\approx 65\text{ wt}\%$, and the Al increased to about $\approx 10\text{ wt}\%$. In the coating layer (above $\approx 19\text{ }\mu\text{m}$), the Fe and Al content did not vary through the thickness at $\approx 55\text{ wt}\%$ and $\approx 40\text{ wt}\%$ respectively. It was also observed that Cr increased to $\approx 25\text{ wt}\%$ at the interface with the aluminised coating, then dropped to a negligible wt. % value in the aluminised top layer.

A similar near surface morphology was observed for the EUROFER-97 coated with the CVD2 process (Fig. 5). However, the higher temperature ($750\text{ }^\circ\text{C}$) induced the formation of a thicker interdiffusion layer ($\approx 40\text{ }\mu\text{m}$), as clearly identified from the Al-L α elemental map in Fig. 5. The deeper interdiffusion layer was also confirmed by local SEM-EDX “spot” analyses. The plot c in Fig. 5 showed a $\approx 40\text{ }\mu\text{m}$ interdiffusion zone (from $\approx 10\text{ }\mu\text{m}$ to $\approx 50\text{ }\mu\text{m}$ below the surface), where Fe dropped from $\approx 87\text{ wt}\%$ to $\approx 50\text{ wt}\%$ and Al increased from $0\text{ wt}\%$ to $\approx 45\text{ wt}\%$. The Cr was observed to be constant at $\approx 10\text{ wt}\%$ in the interdiffusion layer, then dropped to a negligible value in the external Al coating. The plot c of Fig. 5 also contained abrupt changes of the chemical composition, as spikes of Al (light blue dots) and Cr (blue dots) which are associated with the presence of Al-enriched areas, possibly associated with the formation of second phases formed during the CVD process (e. g., at $33\text{ }\mu\text{m}$) and with the presence of Cr-rich M_{23}C_6 carbides [43] at $\approx 8\text{ }\mu\text{m}$, $\approx 11\text{ }\mu\text{m}$ and $\approx 23\text{ }\mu\text{m}$ as second phases in the EUROFER-97 matrix.

Complementary XRD analyses on the CVD1 and CVD2 specimens confirmed the SEM-EDX data. The diffractograms a and b of Fig. 6 showed the peaks of the near surface region associated with the CVD1 and CVD2 process respectively. The data showed the presence of Al_2O_3 , and several intermetallic compounds between Fe and Al, identified as predominantly FeAl₆, and Fe₂Al₅. It is likely that some residue of Al_2O_3 from the powder used for the CVD process was still present after the CVD processes due to the low Gibbs free energy associated with this oxide [44,45], thus explaining the peaks in the diffractograms (Fig. 6). On the surface, no FeAl was detected from the EUROFER-97 coated with the two CVD processes.

EBSD maps showed the near surface microstructural changes of EUROFER-97 after the electroplating (Fig. 7a, b), aluminised CVD1 (Fig. 7c, d) and aluminised CVD2 (Fig. 7e, f) processes. The electroplated process did not induce any microstructural changes in the near surface region of the EUROFER-97, as the pure Al-layer was only deposited on

the EUROFER-97 top surface at room temperature. The IPF-Y map of Fig. 7a showed an elongated structure of the Al grains, where the majority of the grains were oriented along the $\langle 101 \rangle$ direction, whereas the EUROFER-97 presented a randomly oriented grain microstructure [43]. The phase map of Fig. 7b identified the Al layer (light blue) and the Fe bcc (red) phases.

The CVD1 process induced the formation of the external aluminised layer where the grains were preferentially oriented along the $\langle 001 \rangle$ direction, with larger grains observed in the EUROFER-97 just beneath the surface (IPF-Y map in Fig. 7c). The coating was identified as FeAl_{2.8} (blue) with Fe₂Al₅ (pink), as shown in the phase map in Fig. 7d, whereas the EUROFER-97 microstructure was identified as Fe bcc (red) in the phase map in Fig. 7d). The higher temperature associated with the CVD2 process induced the formation of a more evident aluminised coating with small randomly oriented grains in the aluminide layer, and larger randomly oriented grains in the interdiffusion layer (IPF-Y map in Fig. 7e). The smaller grains were identified as FeAl_{2.8} (blue) and FeAl₆ (green), whereas the larger grains were associated with Fe₂Al₅ (pink), as shown in the phase map of Fig. 7f.

Complementary nano-hardness analysis showed that the electroplated layer was softer than the EUROFER-97, as it was formed of pure Al, whereas both CVD processes induced the formation of a hardened Al-Fe layer. The plot a of Fig. 8 show the hardness as function of the different layers for the electroplated, CVD1 and CVD2 coatings. The pure Al-layer associated with the electroplated Al coating showed the lowest hardness value 0.5 GPa , whereas the external layer produced with both CVD processes showed similar hardness values ($\approx 11\text{ GPa}$). Also, the hardness value associated with the interdiffusion layer was similar for both CVD processes ($\approx 4.4\text{ GPa}$). The hardness value of EUROFER-97 was observed to be consistent between the three specimens, and equal to approximately $\approx 3\text{ GPa}$. The modulus is shown in the summary plot b of Fig. 8. The value of the modulus of the pure Al layer was the lowest ($\approx 56\text{ GPa}$), whereas the modulus values associated with the CVD coating layers and EUROFER-97 were comparable and equal to about $\approx 200\text{ GPa}$. The full hardness and modulus data are shown in Table 3. The full data set of hardness and modulus as function of the depth was added as supplementary material and shown in Figure S1.

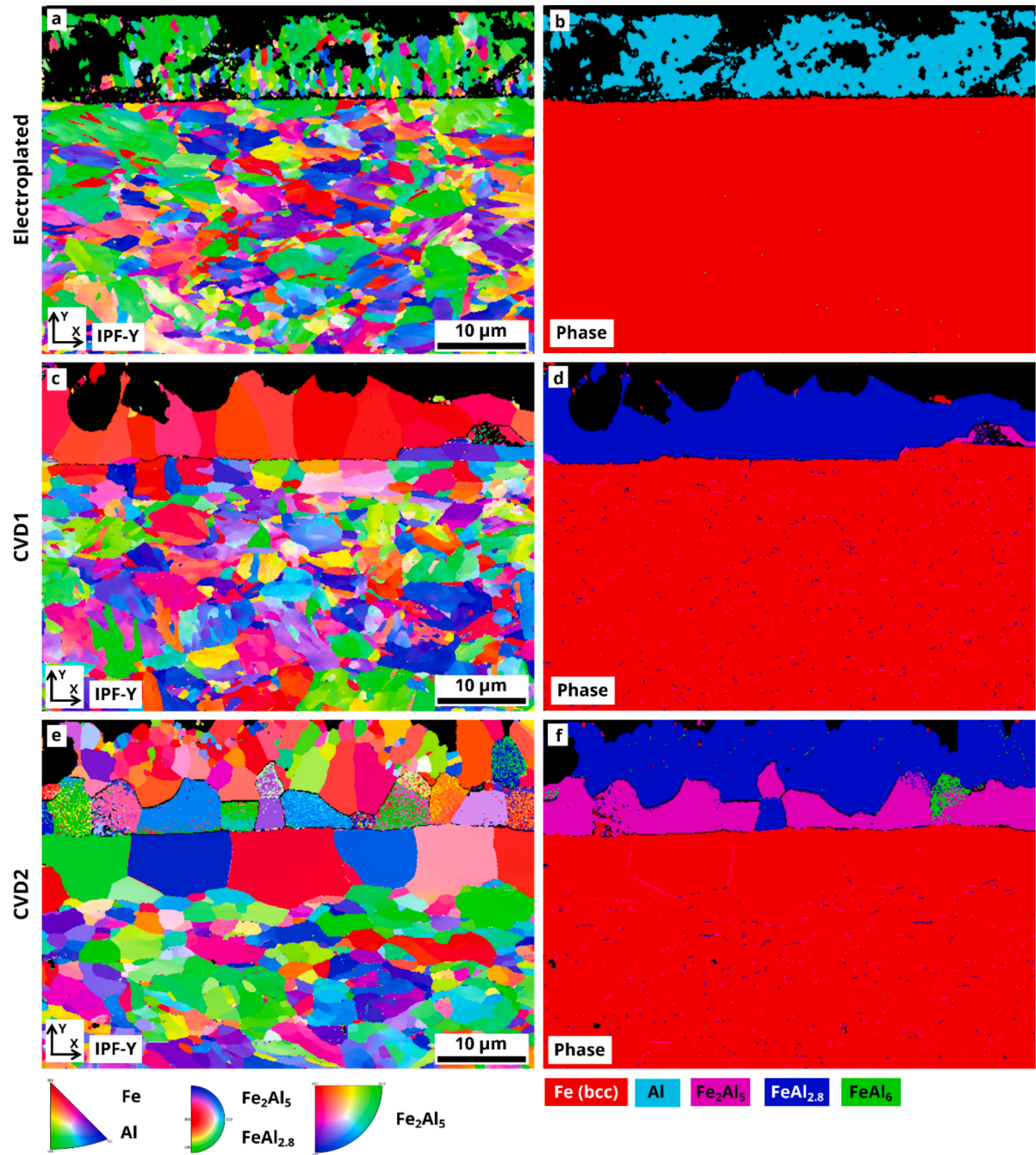


Fig. 7. (a) IPF-Y and (b) phase maps associated with the EUROFER-97 with electroplated Al-coating. (c) IPF-Y and (d) phase maps associated with the EUROFER-97 with the CVD1 Al-base coating, and (e) IPF-Y and (f) phase maps associated with the EUROFER-97 with the CVD2 Al-base coating.

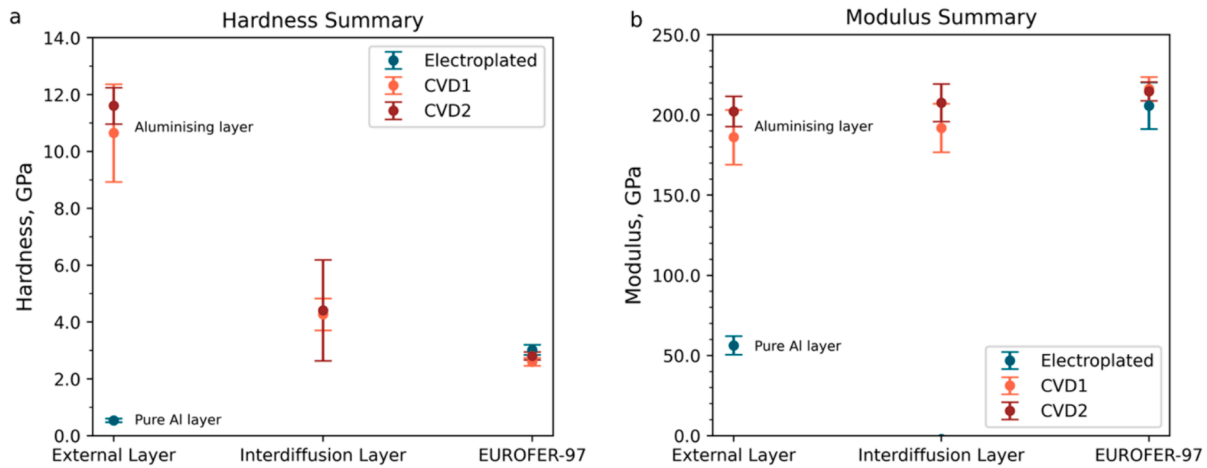


Fig. 8. Hardness-depth curves for the (a) electroplated, (b) CVD1 and (c) CVD2 Al-base coatings for EUROFER-97. (d) Summary of the hardness for the several layers for the electroplated, CVD1 and CVD2 Al-base coatings.

Table 3

Hardness and modulus values for the Al, CVD1, CVD2 coatings and EUROFER-97.

Coating	Layer	Hardness, GPa	Modulus, GPa
Electroplated	Al coatings	0.5 ± 0.1	56.3 ± 5.8
	EUROFER-97	3.0 ± 0.2	205.7 ± 14.5
CVD1	Aluminide layer	10.6 ± 1.7	186.1 ± 17.0
	Interdiffusion layer	4.3 ± 0.6	191.9 ± 15.1
CVD2	EUROFER-97	2.6 ± 0.1	216.2 ± 7.3
	Aluminide layer	11.6 ± 0.6	202.2 ± 9.4
	Interdiffusion layer	4.4 ± 1.8	207.6 ± 11.7
	EUROFER-97	2.8 ± 0.1	214.7 ± 5.8

3.2. Material characterization after straining

The surface and the near surface regions of the SS-J3 type specimens were also characterized to understand the behaviour of the Al-base coating and of the near surface region of EUROFER-97 after straining. Representative SE images of the surface after straining for the electroplated, CVD1 and CVD2 coatings are shown in Fig. 9a, b and c respectively. The surface of the electroplated specimens (Fig. 9a) did not show any cracks or plastically deformed regions, and the morphology of the surface features was comparable to that observed on the specimen before the straining. Instead, the samples from both CVD processes exhibited the formation of large cracks, where the majority appeared to be perpendicular to the loading direction, as indicated from the red arrows in the top SE micrographs of Fig. 9b and c.

The cross-sectional view confirmed the integrity of the electroplated coating. In fact, no cracks or delamination were observed (Fig. 10a). Images of the cross section of the CVD1 (Fig. 10b) and CVD2 (Fig. 10c) coatings confirmed the formation of the cracks.

Further higher magnification SEM-BSE images showed that the cracks stopped within the interdiffusion layer, and the primary crack presented a blunt tip, thus suggesting that only the section with the presence of Al was susceptible to cracking, as shown in Fig. 11, where higher magnification images of the crack regions in the CVD1 (Fig. 11a) and CVD2 (Fig. 11b) coating are shown.

The location of the tips of the primary cracks was also confirmed via SEM-EDX. The Al-K α map and the local spectra extracted from the location s1 and s2 clearly showed that cracks arrested within the Al interdiffusion layer (Fig. 12). Similar findings were observed for the cracks developed in the CVD2 layer (Fig. 13). A total of 47 cracks were identified over 2.12 mm for the CVD1 and 41 for the CVD2, thus leading to a linear crack density of 22.17 no./mm and 19.34 no./mm for CVD1

and CVD2 respectively, indicating a similar behaviour of both the CVD coatings, regardless of the different deposition parameters (supplementary Figure S2).

High magnification GROD maps in the proximity of the cracks are shown in Fig. 14 for both CVD1 and CVD2. For both coatings, it was noticed that the cracks developed transgranularly in the external Al-coating, then transitioned to intergranular in the substrate material which had grains with a bcc structure. The crack behaviour was also confirmed from the GROD angle maps, which showed a low value of misorientation in the top coating area and high value of misorientation within the interdiffusion layer, thus suggesting a plastic deformation around the crack tip while penetrating inside the different Fe-Al layers.

4. Discussion

The aim of this study was to assess the behaviour under strain of Al-base coatings on EUROFER-97 by using electron microscopy and nano-hardness techniques.

4.1. Al-base microstructure

The top view micrographs (Fig. 2) showed the different surface morphologies associated with the different coatings examined in this study. The surface microstructure of both CVD processes is consistent with previous data in literature [46,47]. The surface compounds were identified with microscopy analyses (Fig. 4, Fig. 5, Fig. 7, from Fig. 12 to Fig. 14) and complementary XRD (Fig. 6). The data were consistent with the presence of the intermetallic FeAl_{2.8} (where Al is ≈ 60 wt%) and Fe₂Al₅ which has a chemical composition of ≈ 55 wt% Al [48,49]. The phase diagram for Fe-Al system, also shows the presence of FeAl [23,25,27] for chemical compositions in between 10 wt% and 30 wt% for both temperatures, and therefore it is plausible to assume that this intermetallic is present in the interdiffusion layer (Fig. 4 and Fig. 5), however due to the similar crystal structure and lattice parameters between FeAl [40] and Fe bcc [50], it was not possible to distinguish them by using conventional EBSD, and therefore it was not possible to identify them in the interdiffusion layer. Moreover, it is worth noting that small FeAl_{2.8} enriched areas were identified well below the Al interdiffusion layer in the phase maps associated with the CVD1 (Fig. 7d) and CVD2 (Fig. 7f) processes. These small areas are predominantly located along grain boundaries, and it is very likely that they have been incorrectly indexed by the EBSD detector, possibly due to the presence of intergranular carbides or other precipitates with a similar crystal structure to FeAl_{2.8}. The higher temperature of the CVD2 process promoted a deeper diffusion of Al inside the Fe bcc microstructure [51]. Top surface (Fig. 2)

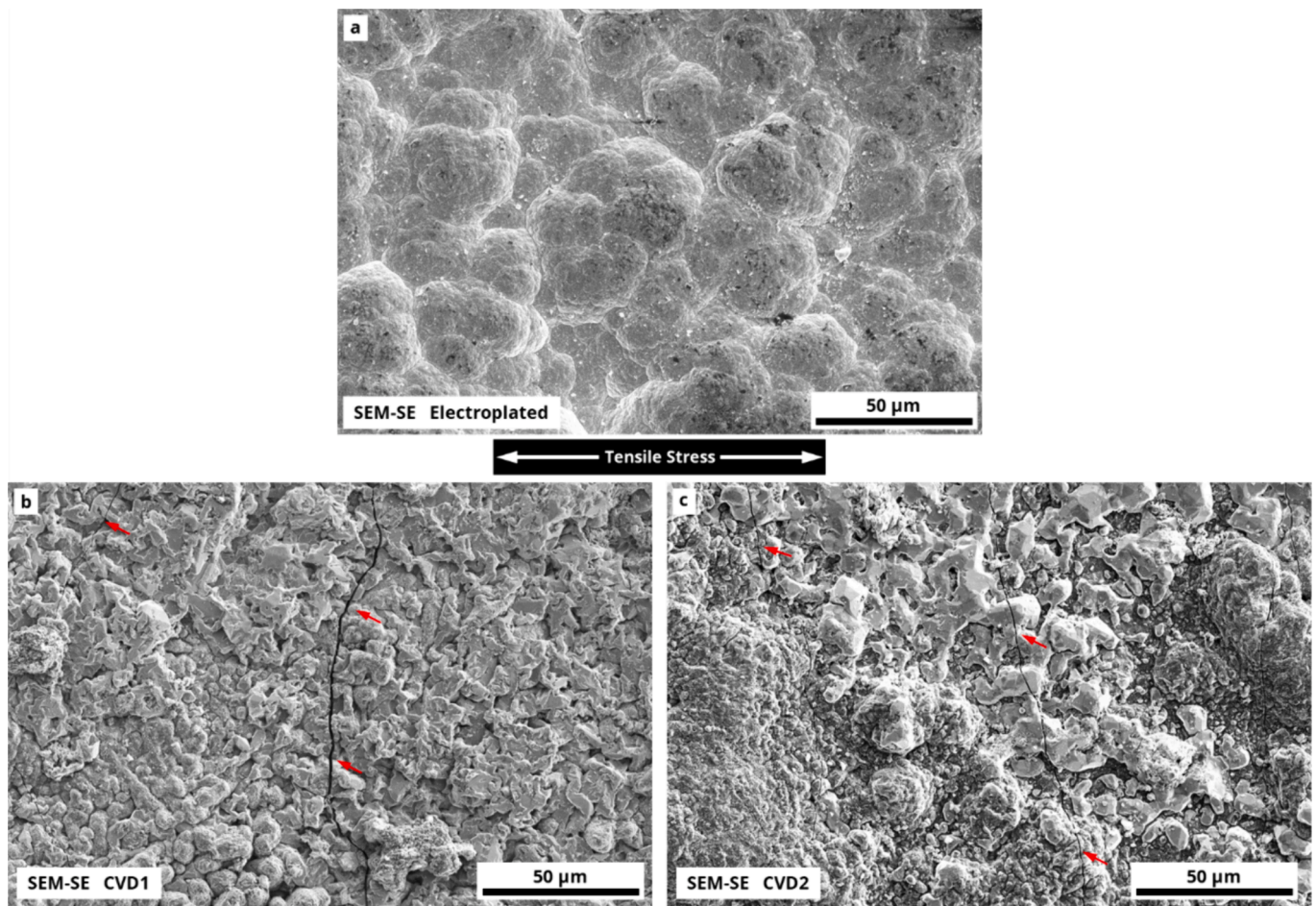


Fig. 9. SE SEM top surface micrographs of the EUROFER-97 with (a) electroplated, (b) CVD1 and (c) CVD2 Al-base layer after engineering straining of $\approx 1\%$. The micrographs showed the presence of cracks (red arrows) perpendicular to the loading direction for both CVD1 and CVD2 coatings.

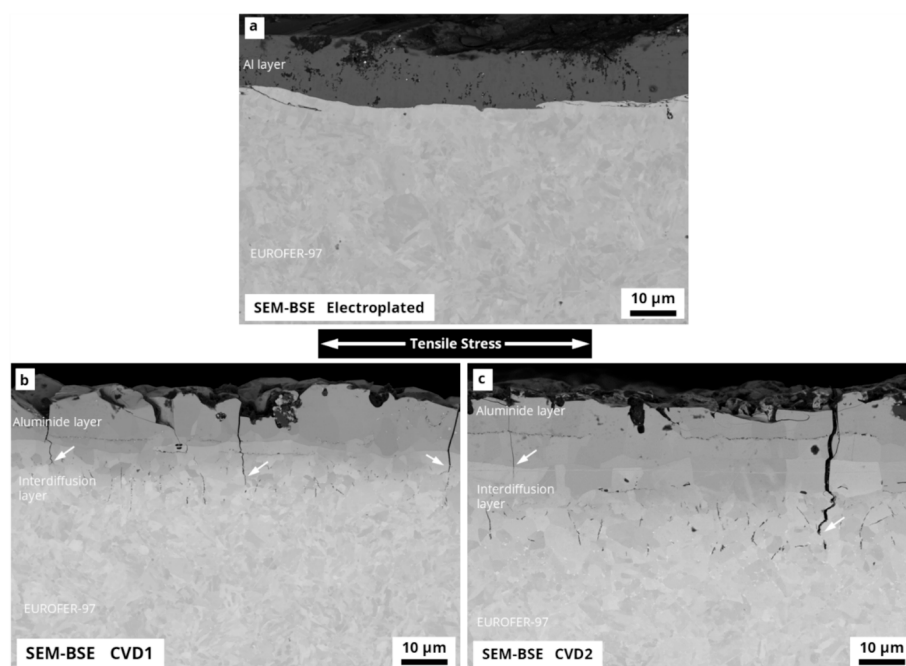


Fig. 10. BSE SEM cross sections micrographs showing the near surface microstructure of the EUROFER-97 after (a) electroplated, (b) CVD1 and (c) CVD2 processes and after engineering straining of $\approx 1\%$. The micrographs confirmed the presence of cracks, extending within the Al-interdiffusion layer for both (b) CVD1 and (c) CVD2 processes.

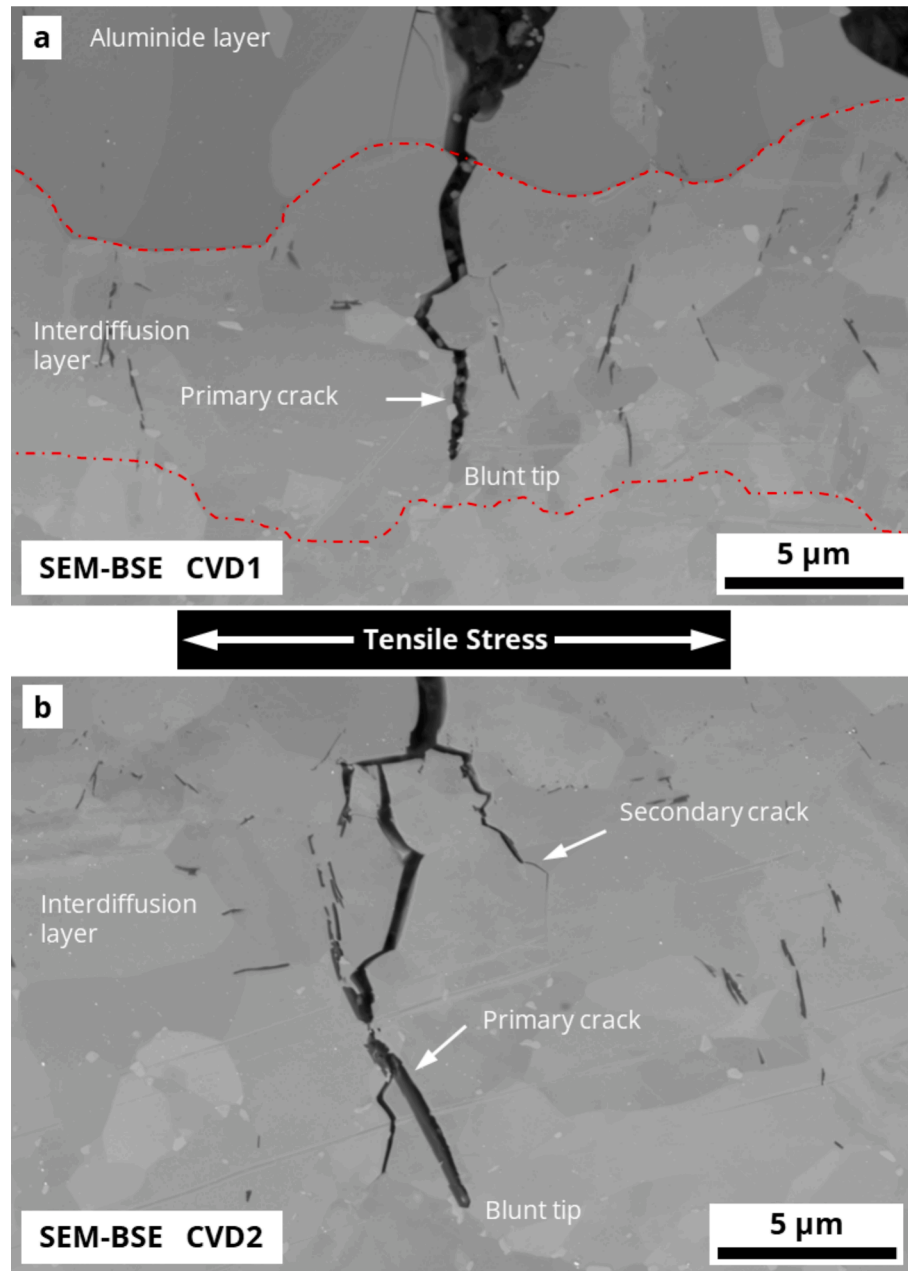


Fig. 11. High magnification BSE SEM cross sections micrographs for the EUROFER-97 after (a) CVD1 and (b) CVD2 EUROFER-97 after engineering straining of $\approx 1\%$. Note the blunt tip of the primary crack for both processes, and the red dashed-dotted lines in (a) separating the aluminide, interdiffusion layer and EUROFER-97. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

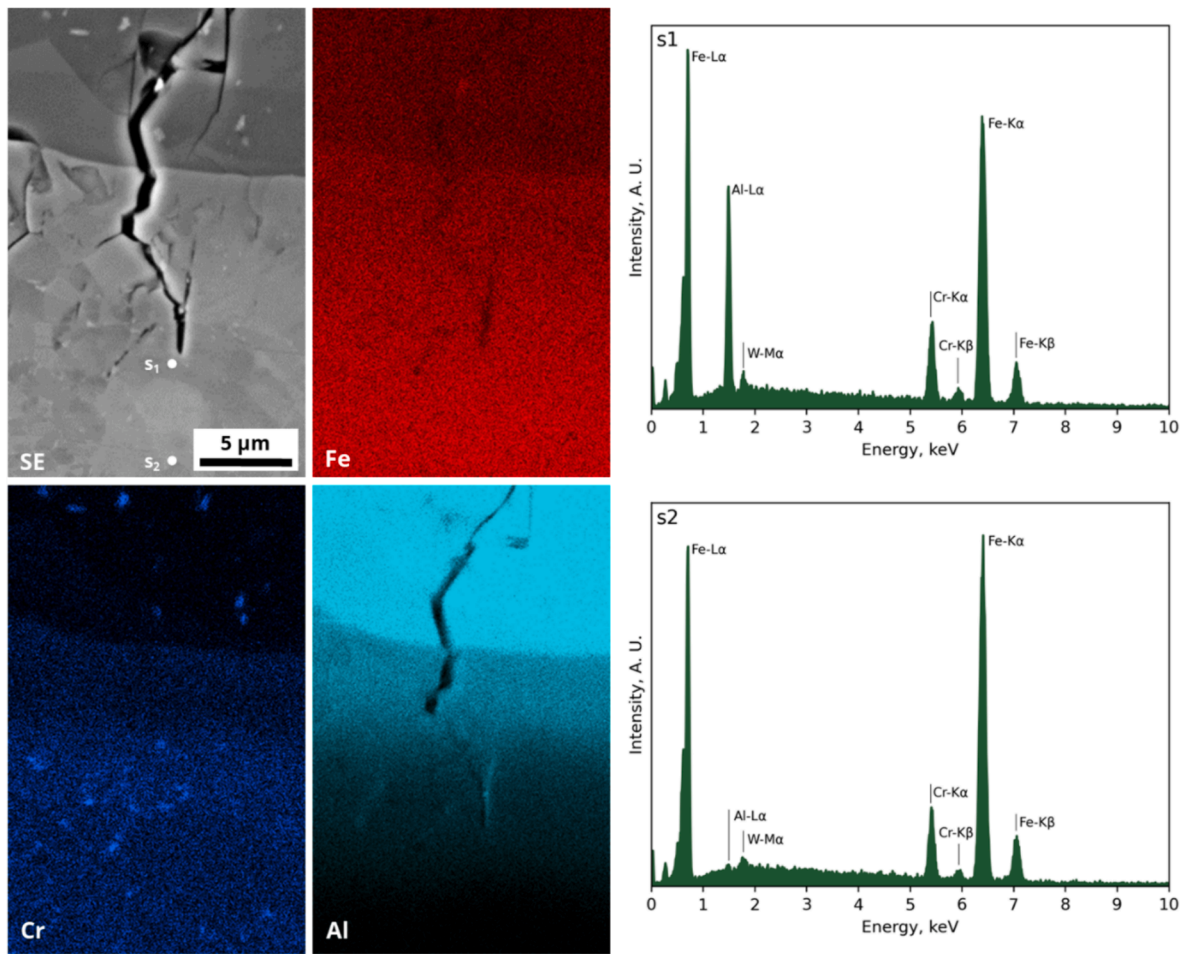


Fig. 12. SE micrograph and corresponding EDX elemental maps for Fe, Cr and Al for the CVD1 EUROFER-97 specimen, showing that the crack tip was located within the Al-interdiffusion zone. A comparison of the Al-L α peaks from the spectra s_1 and s_2 confirmed that the crack stopped within the Al-rich EUROFER-97 near surface region.

and cross sectional micrographs (Fig. 3) also showed the formation of cracks within the aluminised layer, extending up to the interdiffusion layer. It is likely that these fractures are associated with the cooling process of the CVD1 and CVD2 specimens, where the cracks can be associated with the low ductility of the Al-Fe compounds [52].

4.2. Adhesion properties, corrosion protection and H/T barrier layer

No cracks or notable failure along the EUROFER-97-Al interface were observed in the Al coating layer (Fig. 9 and Fig. 10) of the electroplated EUROFER-97 specimen after straining. This behaviour may be described with the higher ductility of Al. On contrary, both CVD surfaces (from Fig. 9 to Fig. 14) appeared to be decorated with cracks that developed perpendicular to the surface. These cracks are likely to have propagated from the pre-existing cracks observed in the baseline material (Fig. 2 and Fig. 3), and possibly formed during the CVD cooling process. The transgranular fracture associated with the cracks in the top-layer of the coating confirms the brittle nature of the top aluminide layer (Fig. 14) [53], whereas, the underneath material associated with the interdiffusion layer and EUROFER-97 shows intergranular cracks with a greater plasticity deformation (Fig. 14) with a blunt crack tip, suggesting

that the bottom area of the interdiffusion layer and EUROFER-97 were not cracked. Despite the poor performance shown in this study, the iron aluminides may still represent a valid solution to improve the resistance to fretting of EUROFER-97; the formation of the cracks is assumed to be associated with some possible residual stresses caused during the cooling process for the two CVD processes and due to the high strain rates used during the strain testing at room temperature. Iron aluminides still represent a commercial valuable alternative as coating as they present good high temperature corrosion resistance under oxidizing environments with the outer hardened layer that can also represent a valid solution against wear and fretting [54–57].

In order to improve the overall performance of the coatings, it is envisaged to clean the surface from any oil contaminants and to reduce the roughness or to achieve a mirror-finish surface. This specific surface will enhance the adhesion properties of the coatings, and specifically for the electroplated layer, it will also mitigate the formation of micro-porosity in the electroplated Al-layer (Fig. 3a). For the CVD process, a cooling process with a more controlled temperature gradient will avoid thermal gradients that can cause the formation of cracking (Fig. 3b and c) in the Al-Fe rich intermetallic layers. It is also worth noting that this Al-layer will subsequently oxidised prior and during service, therefore it

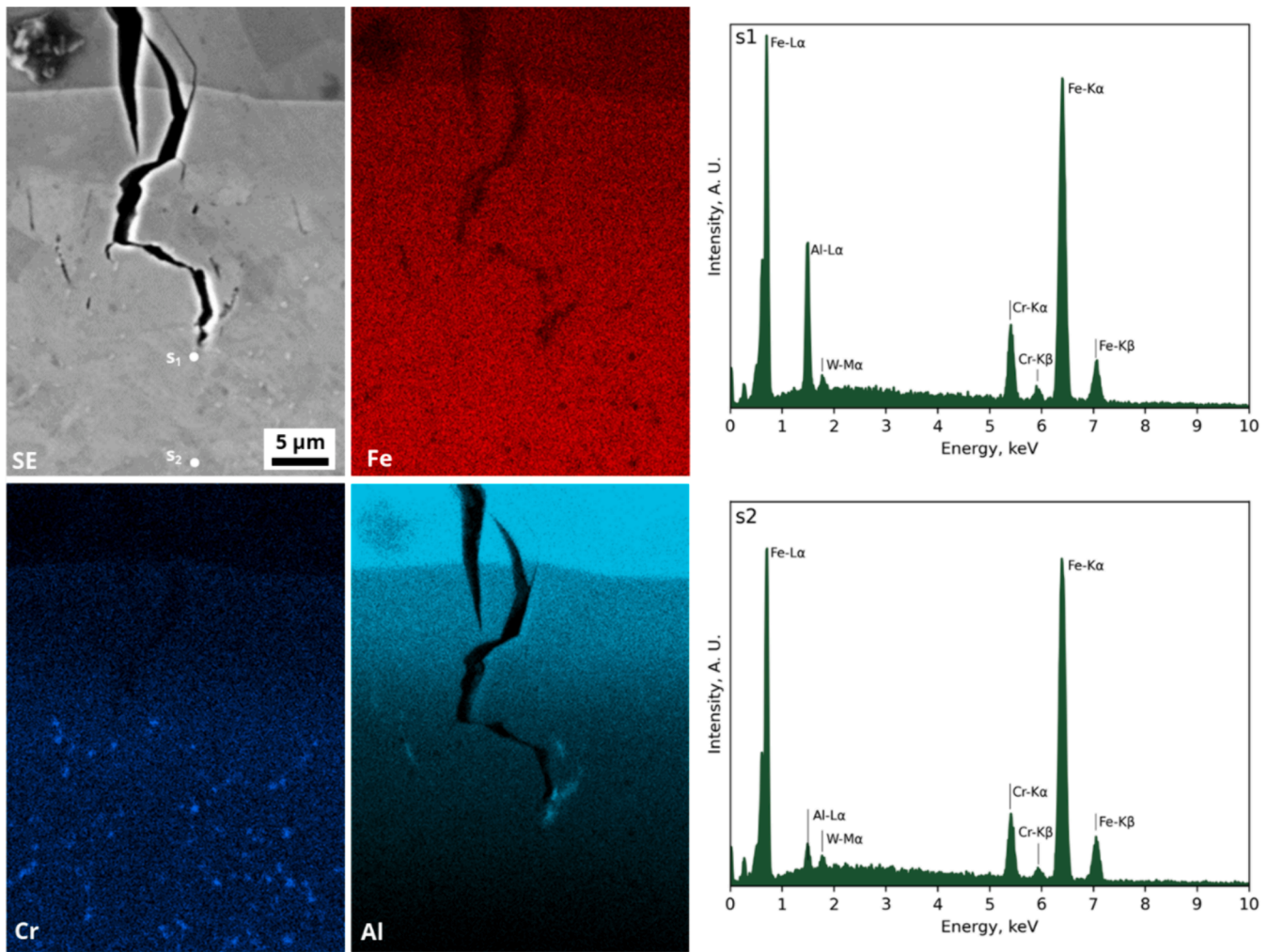


Fig. 13. SE micrograph and corresponding EDX elemental maps for Fe, Cr and Al for the CVD2 EUROFER-97 specimen, showing that the crack tip was located within the Al-interdiffusion zone. A comparison of the Al-L α peaks from the spectra s_1 and s_2 confirmed that the crack stopped within the Al-rich EUROFER-97 near surface region.

is plausible to assume that eventually cracks formed in the aluminide layer will be filled by the formation of Al_2O_3 , thus self-healing the coating during service.

Another important challenge in fusion is to avoid the diffusion of tritium inside the structural material. Tritium represents both a safety and structural concern, associated with the beta radiation and tritium embrittlement of the structural material, therefore efficient confinement of the tritium is a technical challenge. In fact, at the operating temperature of 500 °C, the tritium loss associated with permeation is higher than the natural loss from joints, due to the high permeability of tritium in EUROFER-97 [58]. Currently, Al-base coatings, consisting of either or both aluminide layers and alumina (Al_2O_3) are one of the most promising TPBs for the breeder blanket (BB) sections thanks to their effectiveness in decreasing both hydrogen and tritium permeation and their self-healing and self-passivating properties. Yang *et al.* [14] showed improvement in the reduction of tritium and deuterium by up to 3 orders of magnitude with the formation of $\text{Al}_2\text{O}_3/\text{FeAl}$ on SS 321.

5. Conclusion

This work has assessed the microstructural and mechanical properties of Al-base coatings that can be used as corrosion protection and tritium barrier layer for EUROFER-97. The material was strained at an engineering straining of 1 % and microstructural characterization was performed before and after the straining to assess the performance of the coatings. From this study, the following conclusions can be drawn:

- The electroplated Al formed a uniform layer on the EUROFER-97, whereas the CVD process induced the formation of a rough and corrugated surface with cracks perpendicular to the sample surface.
- The CVD1 and CVD2 processes produced an interdiffusion layer containing $\text{FeAl}_{2.8}$, FeAl_6 and Fe_2Al_5 phases. The higher temperature associated with the CVD2 induced a thicker aluminised and interdiffusion layer, however no improvements of hardness were observed for the CVD2 layer.
- After the straining process, the electroplated coating did not exhibit cracks or delamination along the EUROFER-97 interface. Both CVD1

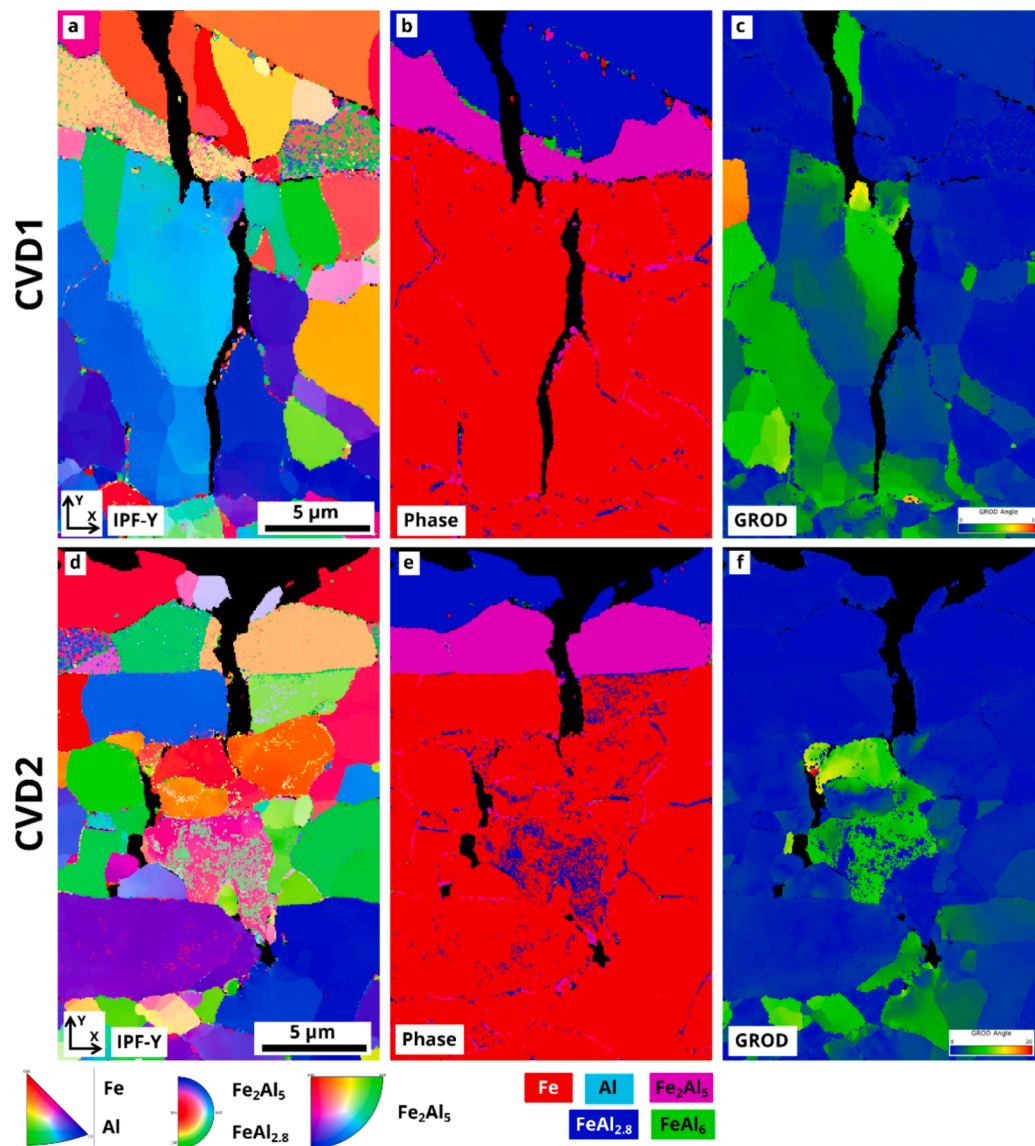


Fig. 14. High magnification EBSD analyses showed the evolution of the near surface region microstructure in proximity of cracks for the (a, b, c) CVD1 and (d, e, f, g) CVD2 EUROFER-97 specimens. The (c, f) GROD maps showed a low misorientation level in the external Al-coating, whereas it increased within the Al-interdiffusion layer.

and CVD2 processes exhibited pronounced cracks following straining, possibly initiated from the thermal cracks associated with the cooling process. The cracks appeared to be transgranular in the external aluminised layer and intergranular in the interdiffusion layer, suggesting a brittle to ductile transition as function of the depth.

- Further oxidation and exposure experiments will be investigated to assess the pre-conditioning oxidising condition of Al-base coatings (either electroplated or CVD) analysed in this study and to support the possible use of these coatings as both corrosion and tritium barrier layers for fusion applications.

CRediT authorship contribution statement

Liberato Volpe: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Tamsin Whitfield:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Luke Hewitt:** Writing – review & editing, Methodology, Formal analysis, Data

curation. **Joven Lim:** Writing – review & editing, Validation, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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(where permitted by UKRI, 'Open Government Licence' or 'Creative Commons Attribution No-derivatives (CC BY-ND) licence' may be stated instead) to any Author Accepted Manuscript version arising. The research used UKAEA's Materials Research Facility, which has been funded by and is part of the UK's National Nuclear User Facility and Henry Royce Institute for Advanced Materials. The authors would like to acknowledge Dr Allan Harte, Dr Rory Spencer and Dr Kurrham Amjad for preliminary discussion on straining methods and for performing the straining of the SSJ-3 type specimens and Diffusion Alloys Ltd for performing the CVD coatings and Ms Lisa Randall and Mr Chris Weekes for invaluable discussion.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nme.2024.101711>.

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