Supplementary information

Corentin Penot

Experimental

Results

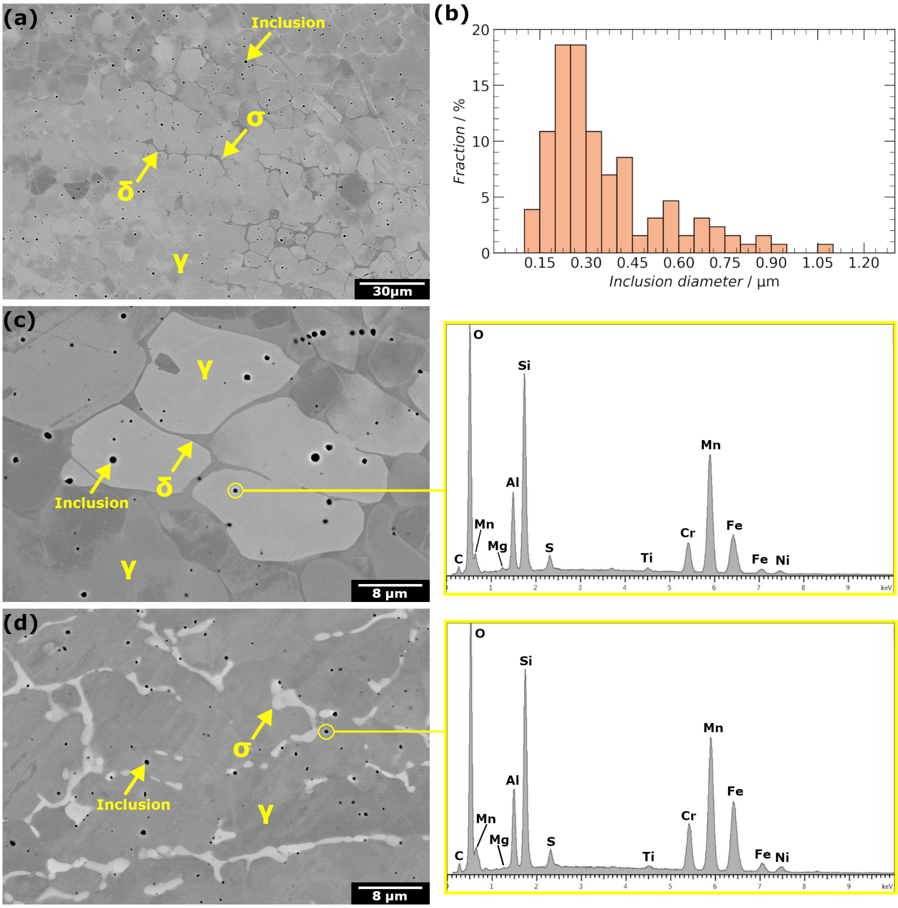

Fig. 1 **(a)** backscattered SEM of as-deposited WAAM 316LSi, **(b)** inclusions size distribution evaluated on 200+ inclusions (bin size 0.05 µm); **(c)**, **(d)**, SEM (BSE) and EDX analysis of an inclusion for the as-deposited and heat-treated WAAM 316LSi, respectively.

EIS fitting

Many EIS equivalent circuits have been proposed to model passive film behaviours based on the known physical structure of the surface oxides and on the nature of the electrochemical reactions at the oxide/solution interface. Three models were tested, namely A [1, 2], B [3] and C [1] (Figure 2) which best corresponds to the experimental data with the minimal number of parameters to avoid over parametrization. Constant phase elements (CPE) were used instead of ideal capacitors to account for the imperfect state of the surface and are characterized by a set of two parameters: Q in (units: Ω^{-1} cm^{-2} s^{n}) and n as a dimensionless exponent, with Q becoming a capacitance for $n = 1$. Model A consists of a modified Randles circuit with a CPE replacing the ideal capacitance and attempts to model a compact oxide film without a hydroxide layer. Model B is akin to model A with the introduction of a porous hydroxide layer: R_1 is associated to the electrolyte resistance inside the pores, CPE_1 corresponds the oxide layer, R_2 estimates the charge transfer resistance of electrochemical processes and CPE_2 accounts for the EDL. Model C divides the passive film into two contributions: an outer hydroxide layer combined with the EDL (*i.e.*, CPE_1, R_1), and an inner oxide layer (*i.e.*, CPE_2, R_2). Mass transport processes were not considered since their influence has been shown to be negligible at similar temperatures [1, 4]. Furthermore, the first analysis of the data does not show diffusion processes at low frequency. Models comparison by fitting the Nyquist plot of specimen AD H is shown in Figure 3 and fit parameters with percentage errors for model A, B and C are summarized in Table 3, Table 4 and Table 5 respectively. The fit obtained using model A, which contains only one capacitive system, was worse than model B and C as shown in Supplementary Figure 2. Additionally, fits had higher χ^2 errors than model B and C, confirming that the system contains more than one capacitive system (*i.e.*, compact oxide film) and requires to take the hydroxide layer into account. A better fit was obtained with models B and C; however, model B had some inconsistencies such as a low n_2 with high errors and high errors for Q_2 and R_2. Conversely, model C had low χ^2 errors, comparable to those of Model B, and the fit parameters were overall more stable with acceptable errors ($<$5%).

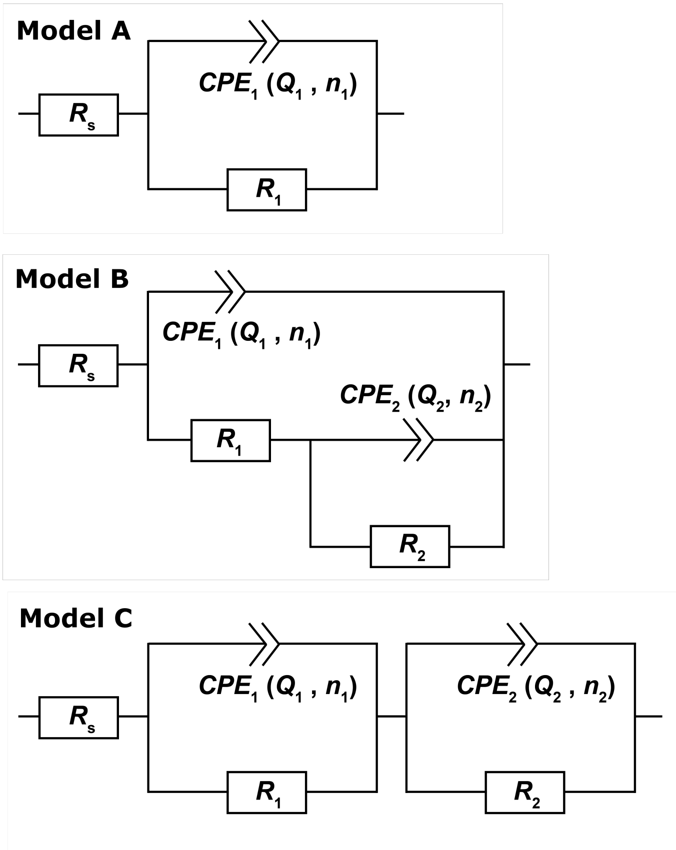

Fig. 2 Equivalent circuits models A, B and C used for EIS data fitting.

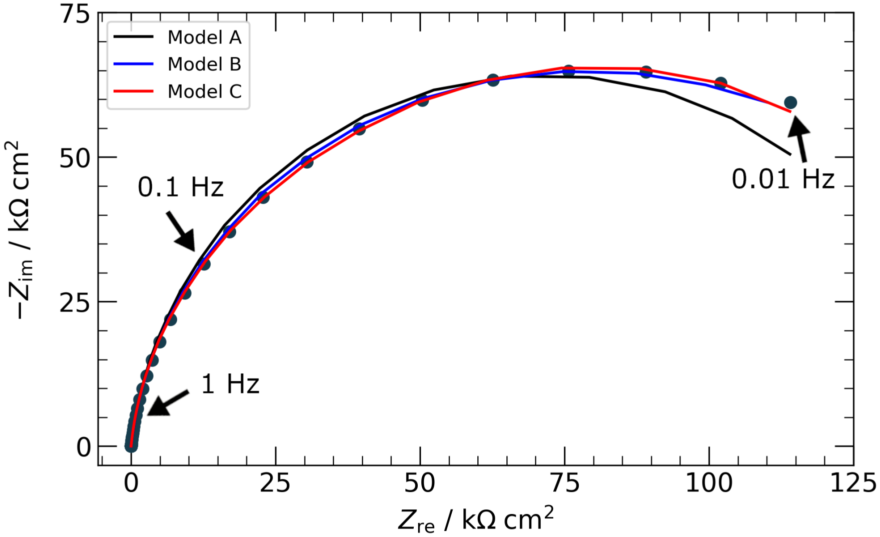

Fig. 3 EIS for WAAM AD H in 3.5 wt.% NaCl solution after 1 h immersion: Nyquist plot fit using model A, B and C.

Linear polarization resistance

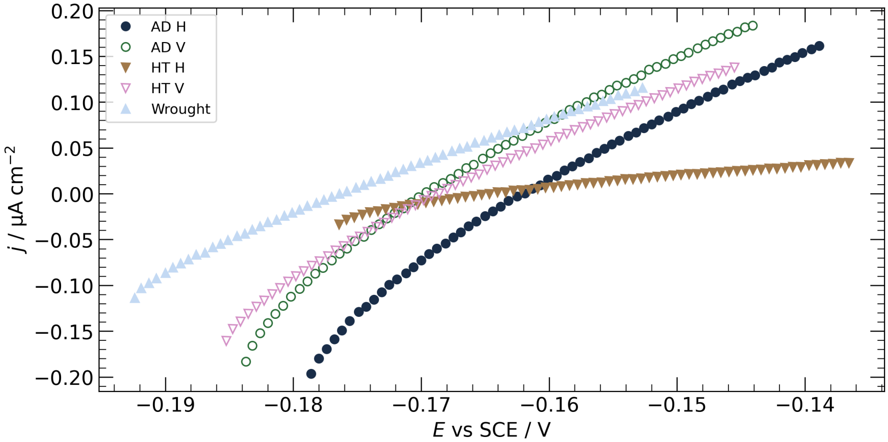

Fig. 4 LPR data for as-deposited WAAM 316LSi, heat-treated WAAM 316LSI and wrought 316L stainless steel in a 3.5 wt.% NaCl test solution (after 1 h immersion, at OCP –0.159, –0.163, –0.155, –0.166 and –0.173 V vs. Ag/AgCl, for AD H, AD V, HT H, HT V and wrought respectively).

References

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[3] Mohammadi, F., Nickchi, T., Attar, M.M., Alfantazi, A.: Eis study of potentiostatically formed passive film on 304 stainless steel. Electrochimica Acta **56**(24), 8727–8733 (2011). https://doi.org/10.1016/j.electacta.2011.07.072

[4] Boissy, C., Ter-Ovanessian, B., Mary, N., Normand, B.: Correlation between predictive and descriptive models to characterize the passive film – study of pure chromium by electrochemical impedance spectroscopy. Electrochimica Acta **174**, 430–437 (2015). https://doi.org/10.1016/j.electacta.2015.05.179

Table 1 MIG/MAG welding torch and robot deposition parameters

Synergic Line in power source	Wire feed speed	Deposition traverse speed	Shielding gas type	Shielding gas flow rate	Torch angle	Average arc current	Average arc voltage
DC pulse	7.0 m min^{-1}	600 mm min^{-1}	98%Ar, 2% CO_2	23 L min^{-1}	90°/90° normal	129 A	12.9 V

Table 2 Chemical composition of the feedstock wire and the build

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Co	Cu	Nb	Fe
Wire	0.010	0.80	1.60	0.010	0.010	18.2	2.50	12.2	-	0.1	-	Balance
Build	0.026	0.79	1.42	0.022	0.005	18.0	2.46	11.2	-	-	-	Balance

Table 3 EIS fitting parameters using model A. Percentage error are indicated within brackets

Parameters	$\boldsymbol{R_s}$ Ω cm^2	$\boldsymbol{R_1}$ kΩ cm^2	$\boldsymbol{Q_1}$ MΩ^{-1} cm^{-2} s^n	$\boldsymbol{n_1}$	$\boldsymbol{\chi^2}$ (10^{-4})
Wrought	16.5 (2.8)	154 (7.2)	38 (2.1)	0.92 (0.5)	44.1
AD H	16.9 (1.3)	143 (2.7)	43 (0.8)	0.93 (0.2)	6.8
AD V	16.7 (1.2)	98 (2.3)	45 (0.8)	0.92 (0.2)	6.1
HT H	19.6 (1.8)	419 (5.3)	27 (1.1)	0.92 (0.3)	12.6
HT V	19.2 (2.6)	149 (4.8)	30 (1.6)	0.91 (0.4)	25.2

Table 4 EIS fitting parameters using model B. Percentage error are indicated within brackets

Specimen	$\boldsymbol{R_s}$ Ω cm^2	$\boldsymbol{R_1}$ kΩ cm^2	$\boldsymbol{Q_1}$ MΩ^{-1} cm^{-2} s^n	$\boldsymbol{n_1}$	$\boldsymbol{R_2}$ kΩ cm^2	$\boldsymbol{Q_2}$ MΩ^{-1} cm^{-2} s^n	$\boldsymbol{n_2}$	$\boldsymbol{\chi^2}$ (10^{-4})
Wrought	16.5 (0.8)	89 (3.0)	34 (0.6)	0.94 (0.1)	497 (43.1)	40 (5.2)	0.51 (3.6)	2.3
AD H	16.9 (0.8)	102 (2.2)	41 (0.5)	0.94 (0.1)	56 (7.7)	44 (14.2)	0.72 (7.6)	1.6
AD V	16.8 (0.8)	77 (1.8)	43 (0.5)	0.92 (0.1)	31 (8.7)	82 (15.5)	0.73 (8.3)	1.5
HT H	19.8 (0.8)	118 (6.1)	26 (0.5)	0.94 (0.1)	416 (4.5)	7.7 (6.2)	0.59 (4.2)	1.3
HT V	19.4 (1.1)	84 (3.0)	28 (0.7)	0.93 (0.2)	76 (5.4)	37 (8.8)	0.93 (3.5)	2.7

Table 5 EIS fitting parameters using model C. Percentage error are indicated within brackets

Specimen	R_s Ω cm^2	R_1 kΩ cm^2	Q_1 MΩ^{-1} cm^{-2} s^n	n_1	R_2 kΩ cm^2	Q_2 MΩ^{-1} cm^{-2} s^n	n_2	χ^2 (10^{-4})
Wrought	16.5 (0.9)	65 (2.4)	47 (0.8)	0.92 (0.2)	165 (7.6)	132 (2.0)	0.96 (0.5)	2.1
AD H	16.9 (0.8)	56 (2.8)	62 (0.8)	0.91 (0.2)	96 (3.6)	117 (1.5)	1.00 (0.5)	1.7
AD V	16.8 (0.8)	39 (2.4)	68 (0.8)	0.9 (0.2)	64 (2.9)	117 (1.4)	0.97 (0.4)	1.4
HT H	19.8 (1.0)	434 (3.5)	36 (0.8)	0.94 (0.2)	21 (10)	103 (2.5)	0.91 (0.5)	2.2
HT V	19.4 (1.0)	146 (2.2)	41 (0.9)	0.93 (0.2)	12 (6.9)	83 (2.1)	0.93 (0.4)	2.2