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Authors
Guo, Pengfei
Lin, Xin
Macdonald, Digby D
et al.

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Unveiling the transpassive film failure of 3D printing transition alloys

Pengfei Guo [a,b], Xin Lin [b,*], Digby D. Macdonald [c,*], Benoît Ter-Ovanessian [d], Jianrui Liu [b], Guangling Song [e], Yufeng Zhang [b], Yongming Ren [f], Hongbo Lan [a], Weidong Huang [b]

[a]*Shandong Engineering Research Center for Additive Manufacturing; Key Lab of Industrial Fluid Energy Conservation and Pollution Control (Ministry of Education), Qingdao University of Technology, Qingdao 266520, China.*

[b]*State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, 127 Youyixilu, Xi'an, Shaanxi 710072, P.R.China.*

[c]*Department of Nuclear Engineering, University of California at Berkeley, Berkeley, CA 94720, USA.*

[d]*Université de Lyon, INSA-Lyon, UMR CNRS 5510 MATEIS, 20 Avenue Albert Einstein, 69621, Villeurbanne, Cedex, France.*

[e]*Center for Marine Materials Corrosion and Protection, College of Materials, Xiamen University, Xiamen, 361005, P.R. China.*

[f]*School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an, Shaanxi 710021, P.R. China.*

**Corresponding author:* xlin@nwpu.edu.cn (X.L.); macdonald@berkeley.edu (D.D.M.).

Abstract

The failure of transpassive films on transition metal alloys was investigated. The results show that the failure of the transpassive film on 3D printing nickel-based superalloy in flowing $NaNO_3$ solution is dominated by self-induced cracking of the film on niobium-segregated phases and the erosion-induced degradation on the film assisted by cation vacancy condensation at the metal/barrier layer interface. Secondary passivation induces the formation of a transpassive film, the nature of which has been debated for decades. The findings are consistent with a bi-layer structure comprising a point-defective barrier layer that grows into the substrate alloy and a precipitated outer layer.

Keywords: A. Superalloys; B. Polarization; B. TEM; C. Anodic dissolution; C. Anodic films; C. Transpassivity;

1. Introduction

Laser solid forming (LSF) is an advanced powder-fed, directed laser energy deposition technology (also known as laser 3D printing or laser additive manufacturing) that can integrate innovative design with integral manufacturing to directly produce difficult-to-cut metal components having complicated geometries and structures (e.g., disks of the aero-engine), which has greatly advanced manufacturing technology [1, 2]. However, the inferior surface quality and poor forming precision of the deposit, caused by the domain-by-domain localized forming features of point-by-point, line-by-line, and layer-by-layer deposition, have significantly limited its further application, and thus subsequent conventional machining is commonly required.

Passivity and transpassivity of metals and alloys are considered to be one of the most important phenomena in electrochemical science [3, 4] and passivity has effectively restrained corrosion by ensuring the kinetic stability of thermodynamically reactive metals, such as Fe, Ni, Cr, Ti, Zr, Al, and so forth. Inspired by the occurrence of transpassive dissolution, electrochemical machining (ECM) has been developed, and widely employed as the subsequent subtractive machining for LSF-parts in recent years [5-7] due to the advantages of no tool wear, no surface hardened layer, and high efficiency. However, the as-deposited parts always exhibit poor ECM performance [8-11] compared to their forged counterparts, at least in the case of nickel-based superalloys comprising transition metals, for example. The improvement of ECM quality represents a significant, ongoing challenge. It is expected that a compact, uniform, possibly porous, and thin transpassive film will lead to the excellent electrochemical machinability quality of metals [12-16] by providing for a uniform electrodissolution current density and therefore uniform metal loss. However, if the transpassive film is susceptible to localized attack, the quality of ECM is compromised because of localized, selective dissolution and the occurrence of a non-uniform electrodissolution current density. Considering the possible chloride attack on the surface film, a chloride-free electrolyte was selected in this study to reveal the nature of transpassive film failure in this study in the absence of that form of attack. Until now, the unexplored mechanism of failure of the transpassive film in chloride-free media remains an important, basic problem in materials electrochemistry, especially for the as-deposited transition metal components with various alloying elements and phases.

It is puzzling that the albeit meager studies of transpassivity, over many decades, including investigation of the formation of transpassive films on transition metals and alloys during ECM processing has not led to a precise understanding of transpassivity, particularly under flowing

electrolyte conditions. This film is commonly referred to as being an “oxide film” [5, 13, 17, 18], an “anodic film” [14, 19], a “corrosion product film” [20] or even a “passive film” [15, 21, 22], even though each of those terms are not exactly synonymous, indicating a lack of precise understanding of the nature of the transpassive state. It is important to note that a distinction must be made between the primary “passive film” that forms at moderate potentials (<1 V vs. standard hydrogen electrode, SHE) and the “transpassive film” (“secondary” passive film) that forms at higher potentials subsequent to the breakdown of the primary passive film. The primary passive film has on a wide variety of metals and alloys in a wide range of environments been studied extensively [3, 23, 24] but little work has been reported on the secondary passive (transpassive) film, as formed during ECM. However, various researchers have investigated transpassive films using spectroscopic analyses (e.g., AES, XPS) and current efficiency measurements, but there are no reports that directly identify the atomic details of the film as a function of the growth conditions (e.g., current density). Although TEM can be used to study the composition and atomic detail of a surface film, the transpassive film is fragile and is easily destroyed during the preparation of TEM specimens. Recently, the emergence of focused ion/electron dual beam systems makes it possible to effectively prepare TEM samples of transpassive film, in spite of the fact that the bombardment effect of the ion beam can enlarge the size of the cracks or micropores existing in the film. In our experience, the *in situ* observation of the evolution of the transpassive film under flowing electrolyte conditions during ECM is very difficult but promises to yield a great deal of information on the nature of the transpassive state.

In the present work, we choose a typical transition metal alloy system with complex microstructural features and phases-one of the most widely used engineering materials, nickel-based Superalloy 718 (Fe-17.83, Cr-18.80, Nb-5.04, Mo-3.00, Ti-0.92, Al-0.44, and Ni-balance

(wt.%), provided by Sulzer Metco of USA) that was prepared by LSF. We report the crystallographic texture, secondary phase particles of the as-deposited Alloy 718. Using aqueous sodium nitrate solution (10wt.%), which is extensively applied in ECM, as the passivating medium, we prepared steady-state transpassive films at different current densities, as well as the steady-state (primary) passive film for comparative study. On the basis of the atomic-scale observations of the transpassive film, we unveil the failure mechanism of the transpassive film. By measuring the potentiodynamic polarization curve from -1 V to 9.8 V (vs. saturated calomel electrode, SCE) and the contrastive study with the primary passive film, we clarify that the formation of the transpassive film during ECM is induced by the formation of the barrier layer of the secondary passive film from the metal substrate rather than the precipitation of dissolution products alone, which is often proposed as a possible mechanism. Our findings may pave the way towards improving the machining precision and surface quality of ECM for highly-alloyed and multiphase 3D printing metals.

2. Materials and Methods

2.1. Material preparation

The bulk Alloy 718 sample was fabricated using a laser additive manufacturing system (LSF-VII). A schematic drawing of LSF is presented in Figure S1A (Note that the figures named Figure S No. are all presented in the Supplementary Materials). The original material used in the LSF experiments is gas-atomized Alloy 718 powders with a particle size range of 45-125 μm (Sulzer Metco, USA). The morphology of the argon gas-atomized powders is shown in Figure S1C. The chemical composition of the Alloy 718 powders is listed as (wt.%): Fe-17.83, Cr-

18.80, Nb-5.04, Mo-3.00, Ti-0.92, Al-0.44, and Ni-balance (provided by Sulzer Metco). The laser processing parameters are as follows: semiconductor laser power of 4 kW, laser spot diameter of 5.3 mm, powder feed rate 30 g/min, scanning speed of 900 mm/min, overlapping ratio of 50%, layer thickness of 0.9 mm, with the scanning pattern of interlayer being staggered. To reduce the cost and to achieve excellent metallurgical bonding, a Q235 substrate (wt.%, 1.40Mn, 0.35Si, 0.22C, ≤ 0.045P, ≤ 0.055S, and Fe balance) was employed. Prior to the LSF experimentation, the Alloy 718 powders were dried in a vacuum oven at 120 ℃ for 4 h to remove the surface absorbed water, so that the powder maintain good flowability. In addition, before the electrochemical experiments, a stress-relief annealing (550℃ for 3 h followed by air cooling) was performed on the deposit to avoid the influence of the residual stress on the electrochemical measurements.

2.2. Electrochemical experiments

Electrochemical experiments consisting of potentiodynamic polarization measurements, potentiostatic current transient analysis, and transpassive dissolution studies were performed on the as-deposited Alloy 718. The potentiodynamic polarization measurements and potentiostatic current transient analyses were performed using an electrochemical workstation (PARSTAT 4000). A typical three-electrode cell was employed, including a working electrode of a cylindrical specimen with an exposed area of 1 cm^2, a square platinum counter electrode (1.5 cm×1.5 cm), and a saturated calomel electrode (SCE). Potentiodynamic polarization was conducted from -1.0 V to 2.5 V (vs. SCE) with a potential sweep rate of 1 mV/s, while the potentiostatic current transients were measured at 0.9 V for 24 hours after stepping the potential from the OCP of -0.5 V. The transpassive dissolution experiments were conducted using an

anodic dissolution device (its image shown in Figure S2) with a high frequency switching direct-current power source (TN-KGZ01 DC 40 V 750 A). During the transpassive dissolution experiments, the electrolyte flow rate was 1.78 m/s.

2.3. Materials characterization

The microstructure of the as-deposited Alloy 718 was observed using scanning electron microscopy (SEM, TESCAN VEGA II-LMH). Crystallographic textures were investigated using SEM with an electron backscatter diffraction (EBSD) system at an accelerating voltage of 20 kV and a step size of 10 μm. The EBSD data was analyzed and displayed by the CHANNEL 5 software. A focused ion/ electron dual beam system (FIB-SEM, FEI Helios NanoLab G3 UC) was used to prepare the transmission electron microscope (TEM) samples of the transpassive and primary passive film, and a high-resolution TEM (HRTEM, FEI Talos F200X) was employed to observe these films.

3. Results

3.1. Microstructure of 3D printing nickel-based superalloy

Alloy 718 samples were prepared by LSF with the powders feeding synchronously resulting in the printing of a rectangular specimen (Figure S1B). Microstructural analysis displays the basic features of the 3D printed, Alloy 718 specimen. On the vertical section (VS), the sample comprises columnar grains approximately along the build direction with a <001> cubic texture and the maximum multiple of the uniform distribution (MUD) value is 9.18 (Fig. 1A and B). Inside the columnar grain, there are numerous secondary phase particles of the Laves phase

($(Ni,Fe,Cr)_2(Nb,Mo,Ti)$) embedded in the Nb-rich region (Fig. 1C and D). The dendrites are equiaxed on the horizontal section (HS) while they are columnar on the VS, suggesting the existence of typical columnar dendrites throughout the structure. Moreover, it is generally acknowledged that there exists significant micro-segregation with Ni, Fe and Cr being enriched in the dendritic trunks while Nb and Mo are segregated into the inter-dendritic region.

3.2. Polarization behavior of 3D printing Alloy 718

We began studying the potentiodynamic polarization behavior of the as-deposited Alloy 718 on HS in sodium nitrate solution to ascertain the ranges of the passive and transpassive regions. As shown in Fig. 2, the curve is typical of the "passivation-transpassivation-secondary passivation" behavior. Once entering in the anodic region, the current density increases slowly with potential, indicating that primary passivation occurs. Beyond 1.09 V, a rapid increase of current density indicates the initiation of transpassive dissolution, possibly coupled with oxygen evolution. However, when the electrode potential is larger than 1.27 V, the current density increases slowly again with potential, suggesting the development of secondary passivation. Beyond 3.79 V, the increase in the current density is probably associated with continued oxygen evolution with the weak potential dependence being attributed to mass transfer control, possibly through a porous, surface deposit (the precipitated outer layer).

3.3. Atomic-scale structure of the primary passive film

Considering that the bl of a steady-state, primary passive film thickness increases linearly with potential [3], a relatively high potential (0.9 V vs. SCE) within the passive region was selected and maintained for 24 hours to obtain a relatively thick barrier layer of the primary

passive film (the current transient shown in Figure S3). It is worth noting that the HS and VS of the deposit both exhibit almost the same steady-state passivation current, and thus we only observe the atomic details of the passive film formed on the HS of the deposit shown in Fig. 3. Note also, that the carbon layer and platinum layer were successively deposited by electron beam and ion beam techniques, respectively (Fig. 3A), to protect the primary passive film from destruction during examination. Using TEM, a compact and polycrystalline primary passive film with a thickness of about 3 nm was found (Fig. 3B), suggesting that the steady-state primary passive film has been formed. Interestingly, a specific secondary phase has been partly embedded in the primary passive film without dissolution, as presented in Fig. 3C, indicating that this secondary phase is electrochemically stable and the outer surface of the passive film dissolves. The observation that the primary passive film is pierced by the secondary phase directly illustrates that the passive film is a meta-stable state, as are all passive films [23], with the steady state reflecting that the rate of formation of the inner (barrier) layer at the metal/film interface being equal to the dissolution rate at the bl/solution (bl/s) interface. The TEM diffraction pattern of the secondary phase (in Fig. 3D) and the interplanar spacing of 0.21 nm (Fig. 3C) both suggest that it is a hexagonal-close-packed structure, C14 Laves phase (Cr_2Nb) with a space group of P63/mmc. In addition, a bi-layer structure of the primary passive film is confirmed (Fig. 3E), with Ni and Cr being enriched in the inner layer while Fe is abundant in the outer layer.

3.4. Transpassive film evolution with current density

Based on the polarization curve shown in Fig. 2, we conducted the transpassive dissolution experiments in the transpassive region with different current densities of 2, 10, 20 and 40 A/cm^2 using an anodic dissolution device (shown in Figure S2) at a flow velocity of 1.78 m/s. While

these are the applied current densities, the current densities involved in passive film growth/dissolution are much less, because most of the current in the transpassive goes to oxygen evolution. Accordingly, the actual current densities involved in passive film growth/dissolution are unknown. Because of the remarkable differences of the surface features (primarily, the surface color) after transpassive dissolution at different current densities (in Figure S4), we chose the transpassive films formed at 2 and 20 A/cm^2 for further analysis. Typically, we only investigate the transpassive films formed on the HS of the deposit to ascertain their surface morphologies and atomic details owing to the same surface features being present on both sections at the same current density (e.g. in Figure S4 A and E, B and F, C and G, and D and H). Fig. 4 presents the top-surface and cross-section morphologies of the transpassive film formed on the HS of the deposit at 2 A/cm^2, as well as its composition analysis. Evidently, some interfacial cracks exist between the dendritic trunks and the inter-dendritic region are distributed on the top-surface of the transpassive film, as shown in Fig. 4A. Curiously, it is the Nb-rich region that these cracks surround, which has been confirmed by the high concentration of Nb in Figure S5. On the cross-section of the specimen shown in Fig. 4B, there exists a recognizable and locally intact transpassive film on the Alloy 718 deposit with an average thickness of about 63 nm. The chemical compositions of the transpassive films along the thickness direction (in Fig. 4C) indicates that the film comprises O, Ni, Fe, Cr and Nb. Obviously, Nb is mainly enriched in the outer layer of the film, which is consistent with the black surface shown in Figure S4A, B, E, and F since the Nb oxides are black [20]. Further, Mo and Ti have not been detected in the transpassive film owing to their relatively low contents or because they have transferred to the electrolyte. It is worth mentioning that the cracks around the Nb-rich region can directly lead to transpassive film rupture by ion beam bombardment during the TEM sample preparation process

and thus it is impossible to observe the intersection between transpassive film and Nb-rich region (including secondary phase) at the atomic scale. Instead, the transpassive film without cracks survives, such as the film formed on the dendritic trunk of the deposit. As it happens, it is on the γ phase that we observe the transpassive film morphology due to the low content of Nb. No doubt, the transpassive film is relatively intact at 2 A/cm^2 except around the Nb-rich region. To study the atomic details of this transpassive film formed at 2 A/cm^2 in depth, high-resolution TEM images and diffraction patterns of the metal/transpassive film interface were obtained, as displayed in Fig. 5. In the high-resolution TEM image (Fig. 5A), the interplanar spacing of 0.209 nm in the metal corresponds to the (1, 1, -1) plane of the γ phase. Furthermore, the incoherent γ phase/transpassive film interface is readily observed, and there exists a plethora of nanocrystals within the transpassive film. The diffraction patterns of the γ phase/transpassive film interface (Fig. 5B) indicates no orientational relationship between the γ phase and transpassive film. Also, the polycrystalline rings (Fig. 5C) suggest that the transpassive film is polycrystalline. Combining these diffraction patterns of the transpassive film with the EDS (Fig. 4C) and XPS results (Figure S6), it is confirmed that the transpassive film is mainly composed of Ni_2O_3, FeOOH, CrO_3, Cr_2O_3, and Nb_2O_5.

Using the same methods, we studied the transpassive film formed on the HS of the deposit at 20 A/cm^2 in sodium nitrate solution. The top-surface and cross-section morphologies of the transpassive film, as well as the elemental distributions, are shown in Fig. 6. The top-surface exhibits an uneven micro-morphology with some cracks around the Nb-rich region (Fig. 6A). In the cross-section view, there exist some evident interfaces and pores (Fig. 6B), preliminarily suggesting that the transpassive film is fractured. To clarify the transpassive film morphology, the elemental distributions maps around the interface of transpassive film and metal are exhibited

in Fig. 6C. Obviously, there exists a metal/carbon interface, indicating the transpassive film has ruptured during ECM at 20 A/cm^2. The dissolution rate anisotropy of the highly textured Alloy 718 on the HS and VS at high current density (in Figure S7) also demonstrates that the transpassive film has been broken. We provide details of a mechanism for the dissolution rate anisotropy in the Supplementary Materials. In addition, the appearance of some pores can be interpreted as indicating that the transpassive film is microporous and that the micropores grow into larger pores by bombardment of the focused ion beam during the TEM samples preparation process, or the local, loose outer layer of the transpassive film was broken by the shear stress generated by the flowing electrolyte and the carbon was directly deposited on the metal by the focused electron beam. Finally, only the parts without pores survive. It is seen that the transpassive film mainly comprises Ni oxide, and other oxides have almost disappeared. More importantly, the transpassive film close to the metal (rectangular box in Fig. 6C) contains more that the stoichiometric ratio of oxygen to metals, indicating that the high concentration of metal cation vacancies condensed at that location. The diffraction pattern of the transpassive film (Figure S8) shows the almost same polycrystalline rings as those of the transpassive film formed at 2 A/cm^2. After calibration and XPS analysis (Figure S9), it is confirmed that the transpassive film is mainly comprises Ni_2O_3 and small quantities of CrO_3, Cr_2O_3, FeOOH, and Nb_2O_5. Obviously, the high current density leads to significant changes in the chemical compositions of the transpassive film.

4. Discussion

The primary passive film exhibits a bilayer structure of an inner Ni-, Cr-rich layer and Fe-rich outer layer (shown in Fig. 3) but the transpassive film at 2A/cm^2 exhibits an almost

homogenous structure and is thicker, indicating that the film is physically and chemically quite different than the primary passive film. With regards to the thickness, it is important to note that the barrier layer of the transpassive film is expected to increase linearly with voltage as imposed by the galvanostatic polarization conditions and as predicted by the PDM [23]. Generally, the barrier (inner) layer of the primary passive films that form on Cr containing alloy is considered to be point defective $Cr_{2+x}O_{3-y}$ containing interstitial substituents of Ni, Fe, and Cr [23]. As a result, the crystalline framework of the barrier layer of the primary passive film that forms on the as-deposited Alloy 718 is that of chromic oxide with the other alloying elements being present substitutionally upon the cation sublattice (e.g., Mo) or (more likely) as interstitials (Cr, Fe, Ni, etc). When Cr(III) oxidizes to Cr(VI), corresponding to the onset of the transpassive region [$Cr_2O_3 + 5H_2O \rightarrow 2CrO_4^{2-} + 10H^+ + 6e^-$], the bl is destroyed and the substrate is immediately covered with another barrier oxide (e.g., Ni_2O_3) that forms in its place and that does not suffer the same fate as Cr_2O_3, at least at this potential. Provided that the mass transfer conditions are favorable, hydroxides and/or oxyhydroxides may precipitate to form an outer layer. The formation of these oxides (barrier layer) and/or hydroxides (outer layer) on the metal surface directly leads to the secondary passivation, this is confirmed by the secondary passivation region in the potentiodynamic polarization curve (Fig. 2). It is highly improbable that the transpassive film forms via adsorption or precipitation of the electrochemical reaction products alone, because the flowing electrolyte increases the diffusion rate of the dissolution products into the bulk solution and effectively transports the undissoved products away from the surface. Importantly, the maximum current upon the initial applied voltage curve (Figure S10) shows that the current density is resistance-controlled during the transpassive process rather than metal cations

diffusion up to a current density of 40 A/cm^2. An increase in the potential above the transpassive breakdown potential results in the development of the secondary passivation or transpassivity. Therefore, it is appropriated to refer this film as the "secondary passive film".

There are two factors leading to the secondary passive film failure. Firstly, the alloy itself. The various alloying elements with larger atomic number readily segregate, resulting in the formation of secondary phases during the solidification of the laser molten pool, which lays the foundation for the generation of local interfacial cracks within the secondary passive film. For the as-deposited Alloy 718, the lattice structures of the secondary passive film vary from the γ phase to the Nb-rich region due to the compositions difference, which leads to poor interfacial bonding. The different dissolution rates of the outer surface of the barrier layer directly causes interfacial debonding, resulting in self-induced cracking. Secondly, the environment. During ECM, the flowing fluid and the electrochemical potential both play a significant role in the secondary passive film failure. The flowing electrolyte can generate shear stresses at the film/solution interface by a "scouring" action to damage the interface, and the effect of the electrochemical potential can be analyzed in terms of the Point Defect Model (PDM). The PDM [3] specifies the condition that must be met for the oxidative depassivation of a surface is given by the inequality,

¿¿ (1)

where ¿¿ and ¿¿ are the rates of formation of the bl at the m/bl interface at zero bl thickness and the rate of dissolution of the bl at the bl/s interface, respectively. While this condition has been used to account for the transpassive breakdown (dissolution) of the primary passive film on nickel-based alloys, such as Alloy 22, and stainless steels, to our knowledge it has never been employed to account for the oxidative destruction of a secondary passive films. As articulated

previously [24], a number of factors may lead to the inequality expressed by Inequality (1), including enhanced dissolution of the bl [large ¿¿ at low pH (acid depassivation), high flow velocity (erosion-corrosion), and abrasion (tribo-corrosion), for example. However, it is the oxidative dissolution of the barrier oxide layer that is the most prevalent reason for depassivation, at least for the transition metals and their alloys that display multiple oxidation states and that have soluble, high oxidation state products. Thus, the existence of a higher oxidation state of the framework cation (Cr) of the bl results in the oxidative formation of high oxidation state oxyanions, such as Cr(VI) in the form of CrO_4^{2-} from a point defective bl like $(CrFeNiMo)_{2+x}O_{3-y}$ [Cr(III)], resulting in the destruction of the layer and hence in depassivation. There is no fundamental reason why Inequality (1) should not apply to all metals and alloys and, indeed, it even accounts for the existence of the active state because it specifies the conditions under which a bl cannot form, even as a metastable state.

It is well-known that at very high potentials, iron undergoes anodic dissolution to form ferrate [Fe (VI), FeO_4^{2-}]. Ferrate (VI) is a powerful oxidizing agent and decomposes in water to evolve oxygen and form Fe_2O_3 ($4FeO_4^{2-}¿+4H_2O \rightarrow 2Fe_2O_3+8OH^-¿+3O_2¿$¿[25]. For this reaction to be thermodynamically spontaneous, the applied potential must be greater than the equilibrium potential for the Fe_2O_3/FeO_4^{2-} couple ($E_{Fe_2O_3/FeO_4^{2-}}$¿), which is more positive than the equilibrium potential (E^e_{OER}) for the oxygen electrode reaction (OER). The formation of ferrate (VI) in concentrated alkaline environments has been extensively studied, primarily because ferrate (VI) is a powerful oxidizing agent that has found use in purifying water and in the destruction of resilient organic compounds [26-29]. The current efficiency for Ferrate (VI) formation is reported to be as high as 40 % at 30 ℃ [26]; the other species being formed are predominantly

O_2 and ferrate (V) (FeO_4^{3-}). However, these species do not form at potentials that are lower than the oxygen evolution potential and hence secondary depassivation is not expected until the potential is displaced into the oxygen evolution region. The transpassive dissolution of iron in highly alkaline solutions has also been attributed to the formation of ferrate (VI) [29] which is consistent with the condition imposed by the PDM [23], as articulated above.

According to the Nernst-Planck equation, the flux of cation vacancies *Jc* within the bl during cation vacancy generation at the bl/s interface via cation ejection from the bl, especially due to the oxidative ejection (e.g., $Cr_{Cr}+4H_2O \rightarrow CrO_4^{2-}¿+V_{Cr}^{3'}+8H^{+}¿+3e^{-}¿$), is given as [30],

$$J_C=-D_C\frac{C_C}{RT}\chi F\frac{\partial\varphi}{\partial x}-D_C\frac{\partial C_C}{\partial x} \quad (2)$$

in which D_C is the diffusivity of the cation vacancy, C_C is the concentration of the cation vacancy ($V_{Cr}^{3'}$), χ is charge of the cation vacancy (-3), $\partial\varphi/\partial x$ is the potential gradient (i.e. the electric field strength, ε), $\partial C_C/\partial x$ is the concentration gradient.

From Eq. (2), the cation vacancy concentration, the potential gradient and the concentration gradient collectively control the flux (magnitude and direction) of the movement of the cation vacancy within the bl but for most barrier layers studied so far, $\partial C_C/\partial x=0$, to a good approximation, expect for a narrow region in the bl at the m/bl interface. Accordingly, the transport of cation vacancies is overwhelmingly via migration that is driven by the electric field strength. The potential gradient within the bl is determined by the defect structure (defect type and concentrations), but is independent of the applied voltage, such that when the applied voltage (V) increases, the potential drop across the bl increases as $\varepsilon\Delta Lss$, where ΔLss is the increase in the bl thickness in response to the increase in the voltage, ΔV. However, the voltage drops across the m/bl and bl/s interfaces are predicted to be $\Delta\phi_{m/bl}=(1-\alpha)\Delta V-\varepsilon\Delta L_{ss}$ and $\Delta\phi_{bl/s}=\alpha\Delta V$,

respectively, for constant pH and temperature, where α is the polarizability of the bl/s interface. The bl thickness can be written as:

$$L_{ss}=\frac{1}{\varepsilon}[1-\alpha-\frac{\alpha\alpha_7}{\alpha_3}\left(\frac{\delta}{\chi}-1\right)]V+G \tag{3}$$

where G is a constant (PDM) and α_3 and α_7 are transfer coefficients for Reactions 3 and 7 of the PDM. The interfacial reactions are shown in Fig. 7.

The importance of the interfacial potential drops is that the rate constants for the reactions that occur at the m/bl (Reactions 1-3) and bl/s (Reactions 4-7) are defined as:

$$k_i=k_i^{00}e^{\alpha_i\gamma\Delta\phi_{m/bl}}\ (i=1\text{-}3) \tag{4}$$

and

$$k_i=k_i^{00}e^{\alpha_i\gamma\Delta\phi_{bl/s}}\ (i=4\text{-}7) \tag{5}$$

where k_i^{00} is the base rate constant and $\gamma=Ff/RT$. Thus, for a system where no change occurs in the oxidation state of the cation upon ejection from the bl ($\chi=\delta$), $\Delta\phi_{m/bl}=0$, because of exact compensation between the effects of ΔV and ΔL_{ss}, the rate of annihilation of cation vacancies at the m/bl interface is independent of the applied voltage but the rate of generation of cation vacancies at the bl/s interface and hence the flux of vacancies across the barrier layer is an exponential function of V. Thus, at some voltage the flux of vacancies arriving at the m/bl interface exceeds the rate of annihilation, resulting in cation vacancy condensation. This is the situation that exists for the primary passive film that leads to passivity breakdown of the bl and the nucleation of pits at a much lower potential within the primary passive region. In the transpassive region, with $\delta>\chi$, the PDM predicts that exact compensation does not occur and that the rate of Reaction 1 is weakly potential dependent. Nevertheless, the potential dependence of Reaction 1 is significantly less than that of Reaction 4, so that cation vacancy condensation at the m/bl interface upon increasing the voltage is still a viable mechanism for depassivation. The

very little Ni but much oxygen present in the secondary passivation film close to the m/bl interface (shown in Fig. 6) indirectly confirms the existence of cation vacancy condensation.

The PDM predicts that $\partial\varphi/\partial x$ is within the bl is independent of the applied voltage, provided that the bl is sufficiently thin (<3 nm) but even for larger thicknesses, which are expected for the barrier layer in the secondary passive film, the constant electric field strength is still a good approximation [31]. Also, the PDM shows that the defect concentrations are independent of distance through the bl, except for a very small region close to the interfaces and hence that in 99 % of the bl thickness $\partial C_C/\partial x=0$, as noted above. Thus, defects migrate, not diffuse through the bl, but they migrate because of the high electric field (ε is typically 1-5 × 10^6 V/cm) [3]. From Eq. (2), we note that the first term on the right side describes the dominant mode of transport (migration) and that the migration flux is proportional to the defect concentration (C_C), the electric field strength (ε), and the defect diffusivity (D_C). The defect concentration within the bl is determined by the rates of cation vacancy generation (Reaction 4) and annihilation (Reaction 1). The rate of generation is very potential dependent, as is articulated above, while the rate of annihilation is potential-independent ($\delta=\chi$) or is only weakly potential dependent ($\chi<\delta$) because of the near compensation of the effects of voltage and bl thickness on the rate constant for Reaction 1. The result is that C_C increases strongly with increasing voltage, because of the strong increase in the rate constant of Reaction 4. The depletion of Cr and Fe in the secondary passivation film (Fig. 6C) verifies the migration is attributed to the electrochemically-mediated ejection of Cr and Fe from the secondary passivation film/solution interface to form FeO_4^{2-} and CrO_4^{2-}, respectively, under the action of the high applied voltage in the transpassive region.

Therefore, we propose that transpassive film failure is dominated by self-induced cracking resulting from Nb-segregation and the erosion-induced degradation via fluid flow shear stress augmented by cation vacancy condensation, which induces the loss of adhesion of the secondary passive film to the substrate. To our knowledge, these mechanisms have never previously been defined for the transition metals or alloys during ECM processing. The universality of this failure mechanism for secondary passivity of transition metals poses a potential threat for the quality of ECM due to selective dissolution. In addition, we clarify that it is the secondary passivation that leads to the formation of the transpassive film, which has puzzled researchers for decades. These observations can greatly advance the development of the ECM of the 3D printing transition alloys.

Finally, the electrochemical aspects of the above mechanism for passivity and transpassivity of Alloy 718 (and other similar alloys) can be understood in terms of a sequence of events as the potential is made more positive into the ECM region, as follows. First, on increasing the potential from the active region, a defective chromic oxide layer containing significant Fe and Ni interstitials forms on the surface and induces primary passivity. When the potential reaches the value at which Cr in Cr_2O_3 (i.e., Cr_{Cr}) is oxidized at the bl/s interface to form CrO_4^{2-} via the reaction $Cr_{Cr}+4H_2O \rightarrow CrO_4^{2-}¿+V_{Cr}^{3'}+8H^{+}¿+3e^{-}¿¿$, the enhanced generation of cation vacancies ($V_{Cr}^{3'}$) results in vacancy condensation at the m/bl interface, thereby preventing the growth of the bl into the metal. Simultaneously, the barrier layer dissolves electrochemically ($Cr_2O_3+5H_2O \rightarrow 2CrO_4^{2-}¿+10H^{+}¿+3e^{-}¿¿$). Thus, the strong potential dependence of the above cation ejection reaction accelerates the decohesion of the barrier layer from the substrate along with the enhanced dissolution rate of the bl is such that, Inequality (1) is satisfied, thereby resulting in the

loss of passivity and the onset of transpassive dissolution. However, as the potential is further increased, a secondary bl forms on the surface probably comprising an oxide of iron (e.g., Fe_2O_3) or nickel (e.g., NiO) but at some higher potential this bl is also destroyed via the reaction (e.g., $Fe_{Fe}+4H_2O \rightarrow FeO_4^{2-}¿+V_{Fe}^{3'}+8H^{+}¿+3e^{-}¿¿$) coupled with enhanced dissolution (e.g., $Fe_2O_3+5H_2O \rightarrow 2FeO_4^{2-}¿+7H^{+}¿+3e^{-}¿¿$) with the result that the same fate befalls the secondary barrier layer as befell the primary barrier layer. This reaction occurs well above the oxygen evolution potential and hence at a potential that is well above that for the destruction of the primary bl, Cr_2O_3. It is also possible that the bl of the secondary passive film comprises an oxide of niobium, such as Nb_2O_3 or Nb_2O_5, in which case it too is destroyed by reactions like $Nb_{Nb}+2H_2O \rightarrow NbO_2^{-}¿+V_{Nb}^{3'}+4H^{+}¿¿$ or $Nb_{Nb}+3H_2O \rightarrow NbO_3^{2-}¿+V_{Nb}^{5'}+6H^{+}¿+e^{-}¿¿$, respectively, coupled with the appropriate electrodissolution reactions at the barrier layer/solution interface. Although the first reaction is not electrochemically mediated, the cessation of bl growth at the m/bl interface due to cation vacancy condensation is sufficient for Inequality (1) to be satisfied, although breakdown may take longer to occur. It is also possible that the bl of the secondary passive film comprises NiO or Ni_2O_3, in which case the bl is destroyed by a combination of cation vacancy/condensation via $¿_{¿}+3H_2O \rightarrow NiO_3^{2-}¿+V_{¿}^{3'}+6H^{+}¿+e^{-}¿¿$, and barrier layer dissolution ($NiO+3H_2O \rightarrow NiO_3^{2-}¿+6H^{+}¿+4e^{-}¿¿$), which are also potential mediated. At this time, insufficient data are available to perform a full thermodynamic/kinetic analysis of depassivation of the type that has been reported for Alloy 22 [23] for Fe, Ni, and Nb, primarily due to the lack of data for the high oxidation state oxyanions of these metals. Beck et al. [29] reported a potentiodynamic reduction peak potential for FeO_4^{2-} of 0.24 V (vs. Hg/HgO) in 1M NaOH or 0.38 V (vs. SHE) in

concentrated NaOH solution (14.3 to 19 M) at 60 °C but, of course, the equilibrium FeO_4^{2-}/Fe_2O_3 could be many tenths of a volt higher. However, as noted by Schryer, et al. [25], ferrate (VI) oxidizes water to evolve oxygen and to produce Fe_2O_3, from which we conclude that $E_{FeO_¿^{2-}¿/Fe_2O_3^e¿}$ is more positive than $E_{O_2/¿_{H_2O}^e¿}$ and $E_{CrO_¿^{2-}¿/Cr_2O_3^e¿}$, thereby fulfilling the condition that the bl of the secondary passive film must breakdown at a potential that is more positive than that for the primary passive film, in concert with the proposed mechanism.

5. Summary and Conclusions

In this work, the transpassive film failure of 3D printing transition alloys (Alloy 718) in chloride-free solution was investigated. The main conclusions are made as follows:

(1) The microstructure of Alloy 718 fabricated by laser solid forming is mainly composed of γ phase, Nb-rich region, and Laves phase. Furthermore, a strong texture is observed with a maximum multiples of uniform distribution (MUD) value of 9.18.

(2) With the increasing of current density, the transpassive film becomes more and more porous and finally ruptures.

(3) It is the secondary passivation induces the formation of a transpassive film. Further, the failure of the transpassive film is dominated by self-induced cracking of the film on niobium-segregated phases and the erosion-induced degradation via shear stress on the film coupled with cation vacancy condensation at the metal/barrier layer interface that results in decohesion of the barrier layer from the alloy substrate.

(4) A mechanism is proposed that postulates that the Cr_2O_3 barrier layer (bl) of the primary passive film that forms at a potential at the end of the active dissolution region of the alloy breaks down via the simultaneous cation vacancy condensation at the metal/barrier layer interface and

the electrodissolution of chromic oxide at the barrier layer/solution interface and is replaced by a secondary barrier layer film (such as NiO/Ni_2O_3, Fe_2O_3, Nb_2O_5) that induces secondary passivation. However, as the voltage is made more positive, this secondary barrier layer also undergoes breakdown, again via a potential-mediated generation of cation vacancies coupled with vacancy condensation of the bl/m interface and oxidative dissolution of the bl.

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Credit, authorship, and contribution statement

Pengfei Guo: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft. **Xin Lin:** Formal analysis, Funding acquisition, Methodology, Project administration, Supervision. **Digby D. Macdonald:** Formal analysis, Supervision, Writing - review & editing. **Benoît Ter-Ovanessian:** Formal analysis, Writing - review & editing. **Jianrui Liu:** Methodology, Data curation. **Guangling Song:** Writing - review & editing. **Yufeng Zhang:** Formal analysis. **Yongming Ren:** Writing - review & editing. **Hongbo Lan:** Writing - review & editing. **Weidong Huang:** Supervision, Resources.

Declaration of Competing Interest

The authors declare no competing financial interests.

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X**References:**

[1] P.F. Guo, X. Lin, J.R. Liu, J.J. Xu, J.Q. Li, Y.F. Zhang, X.F. Lu, N.S. Qu, H.B. Lan, W.D. Huang. Passive behavior of nickel-based superalloys prepared by high-deposition-rate laser solid forming additive manufacturing. Corros. Sci. 177 (2020), 109036.

[2] D.D. Gu, X.Y. Shi, R. Poprawe, D.L. Bourell, R. Setchi, J.H. Zhu. Material-structure-performance integrated laser-metal additive manufacturing. Science. 372 (2021), g1487.

[3] D.D. Macdonald. The history of the Point Defect Model for the passive state: A brief review of film growth aspects. Electrochim. Acta. 56 (2011), 1761-1772.

[4] W. Ye, Y. Li, F. Wang. The improvement of the corrosion resistance of 309 stainless steel in the transpassive region by nano-crystallization. Electrochim. Acta. 54 (2009), 1339-1349.

[5] D. Zander, A. Schupp, O. Beyss, B. Rommes, A. Klink. Oxide formation during transpassive material removal of martensitic 42CrMo4 steel by electrochemical machining. Materials. 14 (2021), 402.

[6] F. Klocke, A. Klink, D. Veselovac, D.K. Aspinwall, S.L. Soo, M. Schmidt, J. Schilp, G. Levy, J.P. Kruth. Turbomachinery component manufacture by application of electrochemical, electro-physical and photonic processes. CIRP Ann-Manuf. Techn. 63 (2014), 703-726.

[7] R. Schuster, V. Kirchner, P. Allongue, G. Ertl. Electrochemical micromachining. Science. 289 (2000), 98-101.

[8] P. Guo, X. Lin, Y. Zhang, J. Li, J. Xu, Y. Ren, J. Liu, H. Yang, W. Huang. Distinction in anodic dissolution behavior of Inconel 718 prepared by different forming technologies. J. Electrochem. Soc. 165 (2018), E546-E555.

[9] J. Li, X. Lin, J. Wang, M. Zheng, P. Guo, Y. Zhang, Y. Ren, J. Liu, W. Huang. Effect of

stress-relief annealing on anodic dissolution behaviour of additive manufactured Ti-6Al-4V via laser solid forming. Corros. Sci. 153 (2019), 314-326.

[10] P. Guo, X. Lin, J. Li, Y. Zhang, M. Song, W. Huang. Electrochemical behavior of Inconel 718 fabricated by laser solid forming on different sections. Corros. Sci. 132 (2018), 79-89.

[11] X. Wang, N. Qu, P. Guo, X. Fang, X. Lin. Electrochemical machining properties of the laser rapid formed Inconel 718 alloy in $NaNO_3$ solution. J. Electrochem. Soc. 164 (2017), E548-E559.

[12] T. Bergs, S. Harst. Development of a process signature for electrochemical machining. CIRP Ann-Manuf. Techn. 69 (2020), 153-156.

[13] K.W. Mao. ECM study in a closed-cell system. J. Electrochem. Soc. 11 (1971), 1876-1879.

[14] K. Mao, J.P. Hoare. The anodic dissolution of mild steel in solutions containing both Cl^- and NO_3^- ions. Corros. Sci. 13 (1973), 799-803.

[15] J.P. Hoare, K.W. Mao, A.J. Wallace. The electrochemical machining of mild steel in $NaBrO_3$ solutions. Corros. Sci. 12 (1972), 571-578.

[16] B. Zhang, J. Wang, B. Wu, X.W. Guo, Y.J. Wang, D. Chen, Y.C. Zhang, K. Du, E.E. Oguzie, X.L. Ma. Unmasking chloride attack on the passive film of metals. Nat. Commun. (2018), 2559.

[17] K.W. Mao, D.T. Chin. Anodic behavior of mild steel in $NaClO_3$ at high current densities. J. Electrochem. Soc. 121 (1974), 191-194.

[18] W. Liu, Z. Luo, M. Kunieda. Electrolyte jet machining of Ti1023 titanium alloy using NaCl ethylene glycol-based electrolyte. J. Mater. Process. Tech. 283 (2020), 116731.

[19] J.P. Hoare, C.R. Wiese. Current efficiency during the electrochemical machining of iron and nickel. Corros. Sci. 15 (1975), 435-440.

[20] D. Wang, Z. Zhu, N. Wang, D. Zhu, H. Wang. Investigation of the electrochemical dissolution behavior of Inconel 718 and 304 stainless steel at low current density in $NaNO_3$ solution. Electrochim. Acta. 156 (2015), 301-307.

[21] J. Wang, Z. Xu, J. Wang, D. Zhu. Anodic dissolution characteristics of Inconel 718 in $C_6H_5K_3O_7$ and $NaNO_3$ solutions by pulse electrochemical machining. Corros. Sci. 183 (2021), 109335.

[22] D. Wang, Z. Zhu, B. He, Y. Ge, D. Zhu. Effect of the breakdown time of a passive film on

the electrochemical machining of rotating cylindrical electrode in $NaNO_3$ solution. J. Mater. Process. Tech. 239 (2017), 251-257.

[23] D.D. Macdonald. On the existence of our metals-based civilization. J. Electrochem. Soc. 153 (2006), B213-B224.

[24] D.D. Macdonald. The Point Defect Model for the passive state. J. Electrochem. Soc. 139 (1992), 3434-3449.

[25] J.M. Schreyer, L.T. Ockerman. Stability of the ferrate(VI) ion in aqueous solution. Anal. Chem. 23 (1951), 1312-1314.

[26] K. Bouzek, I. Rousar. Current efficiency during anodic dissolution of iron to ferrate(VI) in concentrated alkali hydroxide solutions. J. Appl. Electrochem. 23 (1993), 1317-1322.

[27] K. Kerekeš, L. Hrnčiariková, J. Híveš, M. Gál. On the mechanism of electrochemical transpassive dissolution of Fe-based anodes in binary hydroxide media. J. Electrochem. Soc. 161 (2013), C62-C68.

[28] M. Alsheyab, J. Jiang, C. Stanford. On-line production of ferrate with an electrochemical method and its potential application for wastewater treatment – A review. J. Environ. Manage. 90 (2009), 1350-1356.

[29] F. Beck, R. Kaus, M. Oberst. Transpassive dissolution of iron to ferrate(VI) in concentrated alkali hydroxide solutions. Electrochim. Acta. 30 (1985), 173-183.

[30] C.Y. Chao, L.F. Lin, D.D. Macdonald. A Point Defect Model for anodic passive films: I. Film growth kinetics. J. Electrochem. Soc. 128 (1981), 1187-1194.

[31] G.R. Engelhardt, B. Kursten, D.D. Macdonald. On the nature of the electric field within the barrier layer of a passive film. Electrochim. Acta. 313 (2019), 367-377.