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# Improving Adhesion at the Alumina/Zinc Interface by Stainless Steel Buffers

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## Abstract

The weak interaction between zinc and alumina is responsible for a poor performance of anti-corrosive galvanic zinc coatings on modern advanced high strength steels. In this context, we report a theoretical study on the effect of realistic multi-component metal buffers on the adhesion strength of a model  $\alpha$ -alumina(0001)|zinc interface. Relying on results of ab initio calculations on relevant individual oxide|oxide, oxide|metal, and metal|metal interfaces (separation and interface energies), we determine by Monte Carlo simulations the thermodynamically preferred sequence of components in a multi-component buffer, as a function of buffer composition and oxygen conditions. We find that stainless steel buffers considerably enhance the overall strength of the alumina|zinc interface. Most importantly, we show that a partial oxidation of multi-component buffers, which is unavoidable under realistic conditions, does not degrade their performance. This advantageous property relies on the separation of metal and oxide components in the buffer and on the resulting suppression of weakly interacting oxide|zinc, and moderately strong alumina|metal interfaces. More generally, owing to the possibility of selective oxidation and component segregation, multi-component buffers appear as promising solutions for adhesion improvement at weakly interacting metal|oxide interfaces.

## Introduction

Many fundamental studies have been dedicated to the understanding and optimization of the adhesion strength of transition and noble metals on oxide surfaces in view of applications in microelectronics, in engineering of thermal coatings, or for the formation of protective scales. More recently, the adhesive characteristics of metal|oxide interfaces have also been addressed in the context of galvanic zinc coatings, traditionally used for anti-corrosive protection of steels.<sup>1</sup> Indeed, strengthening elements, such as Al, Si and Mn, which are purposely alloyed into advanced high strength steels (AHSS),<sup>2-5</sup> oxidize selectively during the re-crystallization

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7 annealing of cold-rolled steel strips before galvanization. The resulting oxides segregate at  
8 the steel surface and reduce dramatically the adhesion of the anti-corrosive Zn protection.<sup>1,6</sup>  
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10 Typically, an enrichment of steel with more than 1 wt.% aluminum, may lead to the formation  
11 of a quasi-continuous alumina film at the steel surface. This replaces the conventional reactive  
12 Fe|Zn interface<sup>1,7</sup> by a non-reactive interface between Zn and a wide band-gap alumina,  
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14 eventually impeding zinc adhesion in the standard hot-dip galvanization process.  
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19 Despite such a strong applicative interest, the widespread use of sapphire in the growth of  
20 epitaxial zinc oxide layers,<sup>8</sup> and a variety of studies on the interaction of metals with alumina  
21 surfaces,<sup>9-18</sup> the adhesion of zinc has received relatively little attention in the past.<sup>19-24</sup> In  
22 a previous theoretical study, we have shown that the weak interaction of zinc with the most  
23 stable, stoichiometric  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface can only be enhanced by a net surface charge,  
24 due either to surface polarity or to an excess of surface hydroxyls.<sup>21,24</sup> Alternatively, the  
25 introduction of a simple buffer, made of a single more strongly interacting metal such as  
26 Cr, Fe, or Ni, at the alumina|Zn interface has been shown to enhance adhesion due to the  
27 formation of strong interfacial metal-oxygen and metal-zinc bonds. However, since buffer  
28 oxidation systematically reduces the number of such strong interfacial bonds, it produces in  
29 most cases a detrimental effect on adhesion.<sup>23</sup>  
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40 Since a (partial) buffer oxidation cannot be avoided under realistic oxidizing conditions,  
41 the goal of the present study is to investigate the performance of a multi-component buffer.  
42 By tuning its oxidation characteristics, it may be possible to accommodate an oxygen excess  
43 without degrading the overall adhesion. To this end, we focus on a typical stainless steel  
44 buffer and consider the selective oxidation of its Cr and/or Fe components under increas-  
45 ingly oxidizing conditions. The sequence of metal and oxide components within the buffer  
46 is determined by a Monte Carlo (MC) Metropolis optimization, based on interface energies  
47 of individual oxide|oxide, oxide|metal, and metal|metal interfaces obtained from dedicated  
48 Density Functional Theory (DFT) calculations. Such an approach enables to account for  
49 separation, alloying or segregation of the buffer components, to determine the thermody-  
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namically favored sequence of components and interfaces within the buffer, and to identify the least adhesive interfaces.

Besides an adhesion enhancement by the metallic stainless steel buffer, we show that its partial oxidation, associated to the formation of chromium and/or iron oxides, does not degrade its performances. This is principally due to the thermodynamically favored separation of metal and oxide components in the buffer which results in the suppression of weakly interacting oxide|zinc and moderately strong alumina|metal interfaces. Besides their direct interest for the optimization of industrial buffers, our results show that an explicit account for selective oxidation and component segregation in a buffer is necessary for a correct estimation of its adhesion characteristics. Our proposed DFT-based multi-component buffer model provides a robust but simple and efficient tool to tackle this complex situation.

The paper is organized as follows. After presenting the details and settings of *ab initio* calculations and Monte Carlo simulations in Sec. 2, in Sec. 3 we report the values of interface and adhesion energies at all relevant individual oxide|oxide, oxide|metal, and metal|metal interfaces obtained from DFT. Sec. 4 provides and analyzes the composition profiles in metallic or partially oxidized stainless steel buffers, at thermodynamic equilibrium. It highlights the trends in mixing or segregation of their components, and the consequences for the overall interface strength. The discussion in Sec. 5 offers preliminary results to understand the consequences of interfacial diffusion and of Cr- or Ni- enrichment of the buffer.

## Computational methods and settings

The complex equilibrium structure and composition of a realistic multi-component buffer  $Y$ , such as stainless steel, at the alumina|zinc interface are approximated by a sequence of interfaces involving its metal (Fe, Cr, Ni) and oxide ( $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ) components  $X_i$ :  $Y = X_1|X_2|X_3|\dots|X_N$ . Assuming that the interaction between individual interfaces is negligible, the formation energy (with respect to the corresponding bulk materials) of the entire

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6 alumina|Y|zinc system is equal to the sum of the interface energies of the successive individ-  
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8 ual interfaces: alumina|X<sub>1</sub>, X<sub>1</sub>|X<sub>2</sub>, ..., and X<sub>N</sub>|zinc, which can be obtained from dedicated  
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10 small-scale *ab initio* calculations. The global structural optimization of Y is then reduced to  
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12 a search for an optimal sequence of its components X<sub>i</sub> and the strength of the entire system  
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14 is determined by the weakest (the least adhesive) individual X<sub>i</sub>|X<sub>i+1</sub> interface.  
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17 The computational approach thus involves calculations at two different levels. First,  
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19 a DFT-based method is used for a precise estimation of interface and adhesion energies  
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21 associated to all relevant interfaces. Then, a Monte Carlo Metropolis optimization of the  
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23 component sequence in the multi-component buffer is performed.  
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26 **Ab initio calculations.** All calculations on individual interfaces were performed within  
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28 the DFT implemented in VASP (Vienna ab initio simulation package).<sup>25,26</sup> The interaction of  
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30 valence electrons with ionic cores was described within the projector augmented wave (PAW)  
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32 method,<sup>27,28</sup> the Kohn-Sham orbitals were developed on a plane-wave basis set with a cutoff  
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34 energy of 400 eV. The dispersion-corrected GGA (optB88-vdW)<sup>29-31</sup> exchange-correlation  
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36 functional was used to improve the description of adhesion characteristics, especially at  
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38 weakly interacting metal/alumina interfaces, such as between Zn and the stoichiometric  
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40 alumina(0001) termination.<sup>22</sup> Since it has a relatively small effect on the energetic trends,  
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42 we did not employ the GGA+U approach to correct the electronic structure of the oxides  
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44 under consideration.<sup>22</sup> All calculations were spin-polarized and the relative stability of sim-  
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46 ple non-magnetic, ferro- and antiferro-magnetic solutions was systematically tested. The  
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48 self-consistent iterative solution of the electronic Hamiltonian was converged until energy  
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50 differences became smaller than 10<sup>-6</sup> eV. The above settings assure a satisfactory agreement  
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52 between calculated and experimental characteristics of the bulk materials as demonstrated in  
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54 Figure 1, which displays the oxygen conditions under which the metals under consideration  
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56 and their oxides are stable.

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58 Figure 2 shows the models of oxide|oxide, metal|metal, and oxide|metal interfaces used  
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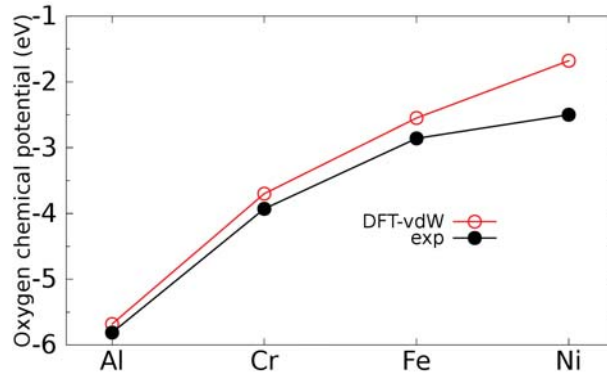


Figure 1: Critical values of oxygen chemical potential above which oxidation of metals is thermodynamically favored.<sup>23</sup> DFT-vdW results are compared to values deduced from the experimental standard enthalpies (per oxygen atom) of oxide formation  $\Delta_f H^0(298.15\text{K})$ .<sup>32,33</sup>

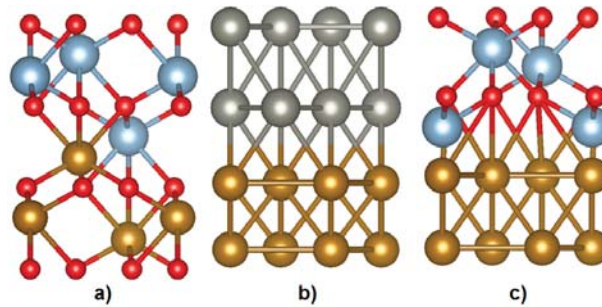


Figure 2: Schematic representation of a) oxide|oxide, b) metal|metal, and c) oxide|metal interfaces. Oxygen atoms are represented by small red balls, cations and metal atoms by large blue and golden balls, respectively.<sup>34</sup>

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7 in the calculations. All calculations on individual interfaces were performed in a superlattice  
8 geometry involving two identical interfaces per periodic unit cell and having the in-plane  
9 lattice parameters fixed to the theoretical bulk alumina ones ( $a = 4.81\text{\AA}$ ). Driven by the  
10  $\text{Al}_2\text{O}_3(0001)$  substrate, a corundum structure was also assumed for chromium and iron ox-  
11 ides and three -M/3O/M- (0001) tri-layers with a  $(1 \times 1)$  in-plane periodicity were used in  
12 superlattice calculations. Conversely, the metal components were represented by seven dense  
13 atomic layers [Cr(110), Fe(110), Ni(111) and Zn(0001)], for which the best in-plane commensurability  
14 with the oxides was provided by a (distorted)  $(\sqrt{3} \times \sqrt{3}) R30^\circ$  unit cell.  
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17 All configurations were thoroughly optimized in a series of structural relaxations starting  
18 from various interface lattice registries. The lattice parameters in the direction normal to  
19 the interface were optimized in order to relax distances between subsequent atomic planes  
20 and positions of all atoms were relaxed until residual forces became smaller than  $0.01 \text{ eV/\AA}$ .  
21 In all calculations, we employed a  $\Gamma$ -centered  $8 \times 8$  Monkhorst-Pack grid for k-point sampling  
22 of the Brillouin zone of the  $(1 \times 1)$  surface unit cell of alumina.  
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25 The interface energy of an individual A|B interface was defined as:

$$26 \quad E_{\text{int}}^{\text{A|B}} = (E^{\text{A|B}} - E_{\text{bulk}}^{\text{A}} - E_{\text{bulk}}^{\text{B}})/2S, \quad (1)$$

27 where  $E^{\text{A|B}}$  is the total energy of the A|B superstructure and  $E_{\text{bulk}}^{\text{A}}$  and  $E_{\text{bulk}}^{\text{B}}$  are the total  
28 energies of bulk materials A and B (with the same in-plane lattice parameters as the super-  
29 structure). Factor 2 accounts for the two equivalent A|B interfaces in the periodic unit cell  
30 and  $S$  is the interface area. Interface energy of an A|A interface is hence equal to zero.  
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33 The adhesion energy at an individual A|B interface was estimated by its separation  
34 energy:  
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$$36 \quad W^{\text{A|B}} = (E^{\text{A|B}} - E_{\text{slab}}^{\text{A}} - E_{\text{slab}}^{\text{B}})/2S, \quad (2)$$

37 where  $E^{\text{A|B}}$ ,  $E_{\text{slab}}^{\text{A}}$ , and  $E_{\text{slab}}^{\text{B}}$  are the total energies of the A|B superstructure and of its isolated  
38 A and B parts in contact with vacuum (with the same in-plane lattice parameters as in the  
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superstructure). We remind that, since interface and adhesion energies are linked by the relationship  $W^{A|B} = \sigma^A + \sigma^B - E_{\text{int}}^{A|B}$  (with  $\sigma^A$  and  $\sigma^B$  the surface energies of A and B),  $W^{A|A} = 2\sigma^A$ .

The effect of a systematic increase of interaction strength by dispersion-corrected exchange-correlation functional on the surface and adhesion energies of some of the materials relevant for the present study has been explicitly estimated in Ref. 22. Here, surfaces energies of metals, alumina, and transition metal oxides are enhanced by about 0.2, 0.3, and 0.4 J/m<sup>2</sup> with respect to the corresponding GGA<sup>35,36</sup> or GGA+U values,<sup>37</sup> respectively. Consistently, adhesion energies are also increased with respect to GGA results (e.g., 0.3 - 0.4 J/m<sup>2</sup> at Zn|alumina and Cr|alumina<sup>22</sup>).

The consequences of the lattice distortion imposed in the calculations can be estimated by comparing surface and adhesion energies obtained with the interface structure matching that of alumina or corresponding to a structural average of the two materials. For example, in the case of Al<sub>2</sub>O<sub>3</sub>|Cr<sub>2</sub>O<sub>3</sub> interface (3% lattice mismatch), surface and adhesion energies change by less than 0.1-0.2 J/m<sup>2</sup>. This difference is somewhat larger (0.2-0.4 J/m<sup>2</sup>) in the case of Al<sub>2</sub>O<sub>3</sub>/Fe (13% lattice mismatch). The impact of the uncertainties due to the choice of exchange-correlation functional and of interface models will be discussed in the following sections.

**Monte Carlo Metropolis simulations.** The MC Metropolis algorithm<sup>38</sup> was used to generate the thermodynamically most favorable sequences of components in the alumina |X<sub>1</sub>|X<sub>2</sub>|X<sub>3</sub>|...|X<sub>N</sub>|zinc superstructure. At each MC step, two randomly chosen components X<sub>i</sub> and X<sub>j</sub> were tentatively exchanged and the new configuration was accepted with probability  $p = \min[1, \exp(-\Delta E/k_B T)]$ , where k<sub>B</sub> is the Boltzmann constant and T is the temperature.  $\Delta E$  represents the change of the total formation energy  $E = E_{\text{int}}^{\text{alumina}|X_1} + E_{\text{int}}^{X_1|X_2} + \dots + E_{\text{int}}^{X_N|\text{zinc}}$  induced by the exchange. In the present simulations, we have used T = 1500 K (k<sub>B</sub>T/S ~ 0.1 J/m<sup>2</sup>) and 20 × 10<sup>6</sup> MC steps and the results were averaged after a system equilibration of 10<sup>6</sup> steps.

As to represent a realistic composition profile of the buffer and to enable mixing and/or separation of each of its components, the latter were represented by several replicas each and the position of each replica was independently optimized. Typically, the stainless steel buffer was represented by 12 Fe, 2 Cr, and 2 Ni replicas, which corresponds to its typical composition 75%Fe, 12.5%Cr, and 12.5%Ni. Each oxide component was represented by two replicas. The possible diffusion of Zn into the buffer was accounted for by the addition of one replica of Zn. The convergence of the results was tested by simulations in which the number of replicas of each component was doubled.

## Results: Energetics of individual interfaces

In this section, we report the results on interface and adhesion energies at the individual interfaces, obtained from *ab initio* calculations. All relevant oxide|oxide interfaces ( $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ ), metal|metal (Cr, Fe, Ni and Zn) and metal|oxide interfaces are considered.

**Table 1: Interface  $E_{\text{int}}$  ( $\text{J}/\text{m}^2$ ) and adhesion  $W$  ( $\text{J}/\text{m}^2$ ) energies at individual oxide|oxide interfaces.**

	$\text{Al}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$
$E_{\text{int}}$			
$\text{Al}_2\text{O}_3$	0.00	0.38	0.43
$\text{Cr}_2\text{O}_3$	0.38	0.00	0.17
$\text{Fe}_2\text{O}_3$	0.43	0.17	0.00
$W$			
$\text{Al}_2\text{O}_3$	3.88	3.57	3.02
$\text{Cr}_2\text{O}_3$	3.57	4.02	3.35
$\text{Fe}_2\text{O}_3$	3.02	3.35	3.04

**Oxide|oxide interfaces.** Interface energies of all oxide|oxide interfaces are found to be small and positive ( $< 0.5 \text{ J}/\text{m}^2$ ), Tab.1. This is consistent with the fact that no change in the number of metal-oxygen bonds or in the cation oxidation state occurs when the

interface is formed from the two bulk materials. Interface energies of  $\text{Al}_2\text{O}_3|\text{M}_2\text{O}_3$  ( $\text{M} = \text{Cr}$  and  $\text{Fe}$ ) are the largest due to a larger structural mismatch and to a noticeable difference in the cation-oxygen bond iono-covalent character between  $\text{Al}_2\text{O}_3$  and the transition metal oxides. Conversely, the interface energy of the  $\text{Cr}_2\text{O}_3|\text{Fe}_2\text{O}_3$  interface is the smallest owing to the structural and bonding similarities of the two oxides. Since the interface energies are small, the adhesion energies roughly scale with the sum of the surface energies of the two components:  $W^{\text{A|B}} \sim \sigma^{\text{A}} + \sigma^{\text{B}}$ . As a consequence, we find a strong adhesion (3-4 J/m<sup>2</sup>) at all oxide|oxide interfaces upon consideration, Tab. 1.

**Table 2: Interface  $E_{\text{int}}$  (J/m<sup>2</sup>) and adhesion  $W$  (J/m<sup>2</sup>) energies at individual metal|metal interfaces.**

	Cr	Fe	Ni	Zn
$E_{\text{int}}$				
Cr	0.00	-0.50	-0.36	-0.51
Fe	-0.50	0.00	-0.51	-0.30
Ni	-0.36	-0.51	0.00	-0.73
Zn	-0.51	-0.30	-0.73	0.00
$W$				
Cr	4.14	4.69	4.44	3.11
Fe	4.69	4.24	4.64	2.95
Ni	4.44	4.64	4.02	3.27
Zn	3.11	2.95	3.27	1.06

**Metal|metal interfaces.** Metal|metal interfaces are also characterized by relatively small interface energies ( $|E_{\text{int}}| \leq 0.7$  J/m<sup>2</sup>), Tab. 2, which is consistent with the absence of substantial structural (bond number) or chemical (oxidation state, bond iono-covalent character) changes upon interface formation. However, contrary to the case of oxide|oxide interfaces, negative values of  $E_{\text{int}}$  are found, which indicate a tendency for alloying, especially well pronounced at the Ni|Zn interface. Similarly to the case of oxide|oxide interfaces, the adhesion energies roughly scale with the sum of the surface energies of the two components, resulting in a strong adhesion (3-4 J/m<sup>2</sup>) at nearly all metal|metal interfaces, Tab. 2. The only exception is the Zn|Zn interface, with a particularly small adhesion energy ( $\sim 1$  J/m<sup>2</sup>), which

originates from the small surface energy of Zn. Representative for the strength of the zinc film itself, we will refer to this value in the following discussion.

**Table 3: Interface energies  $E_{\text{int}}$  ( $\text{J}/\text{m}^2$ ) and adhesion energies  $W$  ( $\text{J}/\text{m}^2$ ) at individual oxide|metal interfaces.**

	Cr	Fe	Ni	Zn
$E_{\text{int}}$				
$\text{Al}_2\text{O}_3$	2.01	2.16	2.10	1.82
$\text{Cr}_2\text{O}_3$	1.72	1.13	1.42	1.52
$\text{Fe}_2\text{O}_3$	-1.21	0.15	0.51	0.79
$W$				
$\text{Al}_2\text{O}_3$	2.00	1.90	1.85	0.65
$\text{Cr}_2\text{O}_3$	2.36	3.00	2.60	1.02
$\text{Fe}_2\text{O}_3$	4.79	3.48	3.01	1.25

**Oxide|metal interfaces.** The energetics of oxide|metal interfaces qualitatively differs from that of oxide|oxide and metal|metal ones. In most cases,  $|E_{\text{int}}|$  values are large (1-2  $\text{J}/\text{m}^2$ ) due to a change of both the number/type of bonds and of the cation oxidation state upon interface formation. Indeed, the formation of a  $\text{M}_2\text{O}_3|\text{M}'$  interface involves breaking  $\text{M}-\text{O}$  bonds and forming  $\text{M}'-\text{O}$  ones. The trend for a progressive increase of  $E_{\text{int}}$  along each line and its decrease along each column in Tab. 3 are well accounted for by the changes of the enthalpies of metal oxidation, Figure 1. In particular, the largest positive  $E_{\text{int}}$  are obtained when strong bonds ( $\text{Al}-\text{O}$ ) are replaced by weaker ones ( $\text{M}-\text{O}$ ). Conversely, the most negative value corresponds to a replacement of relatively weak ( $\text{Fe}-\text{O}$ ) bonds by stronger ( $\text{Cr}-\text{O}$ ) ones, actually highlighting the instability of the  $\text{Fe}_2\text{O}_3|\text{Cr}$  interface with respect to the  $\text{Cr}_2\text{O}_3|\text{Fe}$  one. Finally, a close to zero  $E_{\text{int}}$  value is found at the  $\text{Fe}_2\text{O}_3|\text{Fe}$  interface where no change of the number/type of bonds or cation oxidation state takes place.

Adhesion energies at oxide|metal interfaces are moderate to large (2-5  $\text{J}/\text{m}^2$ ), except in the cases of  $\text{M}_2\text{O}_3|\text{Zn}$ , where large interface energies and small zinc surface energy lead to a weak adhesion, of the order of 1  $\text{J}/\text{m}^2$  only. In particular, zinc adhesion at the alumina (0001) surface is very weak (0.65  $\text{J}/\text{m}^2$ ) and representative for the observed bad adhesion of

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6 anti-corrosive zinc coatings at the surfaces of advanced high strength steels. We will refer to  
7 this value in the following discussion.  
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10 We stress that the discussed qualitative differences in interface energetics of oxide/oxide,  
11 metal/metal, and oxide/metal interfaces reflect the very different nature of these objects  
12 and go well beyond effects due to either a choice of exchange-correlation functional or an  
13 approximate treatment of interface strain effects.  
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18 To summarize, *ab initio* results allow drawing an early picture of the expected behavior  
19 of the various components of a multi-component buffer. On the one hand, the negative  $E_{\text{int}}$   
20 obtained at metal|metal interfaces suggest a systematic tendency for alloying of the metallic  
21 components. On the other hand, positive values for most oxide|oxide and oxide|metal inter-  
22 faces will lead to a reduction of the number of such interfaces and will drive a separation of  
23 the oxide and metal components. As far as the strength of individual interfaces is concerned,  
24 adhesion energies obtained for oxide|oxide and for most metal|metal interfaces (except Zn|Zn)  
25 are systematically large. Oxide|metal interfaces (except oxide|Zn) are also characterized by  
26 relatively large adhesion energies, especially in the case of  $\text{Fe}_2\text{O}_3$ |metal. Since the overall  
27 junction strength is determined by the weakest interface formed in the buffer, these results  
28 suggest that any attempt to strengthen the interface has to aim at eliminating all oxide|zinc  
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## 45 **Results: Equilibrium structure of multi-component buffers**

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47 In this section, we determine the component sequence in a multi-component buffer at ther-  
48 modynamic equilibrium, by MC optimization. We consider a typical stainless steel buffer  
49 of average composition 75% Fe, 12.5% Cr, and 12.5% Ni, under three different oxidizing  
50 conditions, Figure 1: a) oxygen-lean conditions under which the buffer remains metallic, b)  
51 oxygen-moderate conditions under which Cr is partially oxidized, and c) oxygen-rich con-  
52 ditions under which the Cr component is fully oxidized and Fe is partially oxidized. The  
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possibility of zinc diffusion from the coating towards the buffer is accounted for by adding a Zn component in the buffer. In all cases, the spatial distribution of the relevant metal and oxide components and the probability of formation of individual interfaces are determined and the weakest adhesive interface is identified. We first consider a self-standing stainless steel buffer, which is subsequently inserted at the alumina|zinc interface.

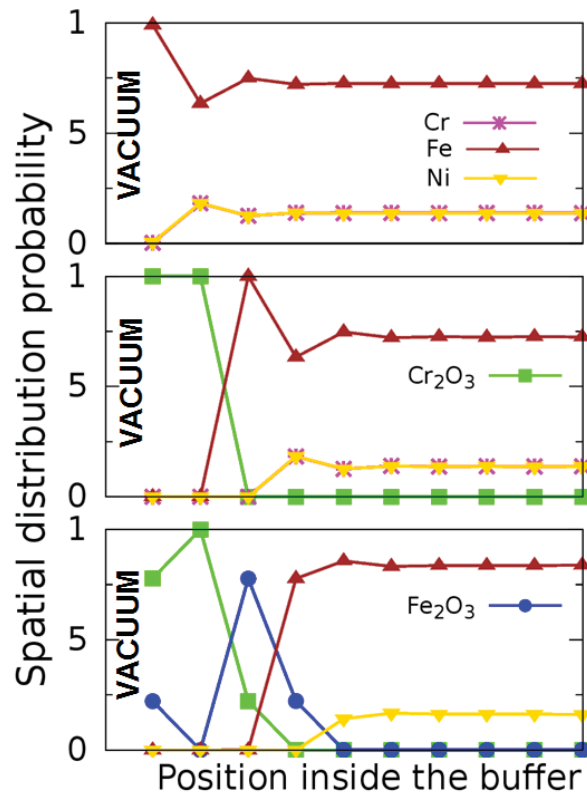


Figure 3: Spatial distribution of components in a self-standing stainless steel buffer in oxygen-lean (top), -moderate (middle), and -rich (bottom) environments.

**Self-standing stainless steel buffer.** Figure 3 displays the spatial distribution of components in a self-standing stainless steel buffer under the three considered oxidizing conditions. In all cases, in the buffer center (right-hand side of the diagrams), the metallic components (Fe, Cr, and Ni) form an alloy with a composition close to that expected from the average buffer one.

In an oxygen-lean environment (buffer composed only of Fe, Cr, and Ni), Fig. 3 (top),

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7 the surface gets enriched in Fe, although Cr and Ni have lower surface energies. This comes  
8 from the fact that these two metals have a strong preference to alloy with Fe, Tab. 2, which  
9 makes them more stable in the buffer core, as long as Fe is largely in excess.  
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12 In an oxygen-moderate environment (buffer composed of Fe, Cr, Ni, and  $\text{Cr}_2\text{O}_3$ ), Fig.  
13 3 (middle), the  $\text{Cr}_2\text{O}_3$  component segregates to the surface, thus limiting the number of  
14 chromia|metal interfaces, as expected from their relatively large  $E_{\text{int}}$ , Tab. 3. This separation  
15 corresponds to the known sacrificial Cr oxidation which prevents oxygen diffusion into the  
16 stainless steel and thus protects it from further corrosion. Below the superficial chromia film,  
17 the buffer is enriched in Fe which ensures a good adhesion to the protective oxide film.  
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24 In an oxygen-rich environment (buffer composed of Fe, Ni,  $\text{Cr}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ ), Fig. 3  
25 (bottom), the situation remains similar, but since most  $\text{Fe}_2\text{O}_3$  segregates at the chromia|Fe  
26 interface the oxide|buffer interface switches from  $\text{Cr}_2\text{O}_3|\text{Fe}$  to  $\text{Fe}_2\text{O}_3|\text{Fe}$ , which strengthens  
27 the entire system even more [ $W(\text{Cr}_2\text{O}_3|\text{Fe}) = 3.0 \text{ J/m}^2$ ) and  $W(\text{Fe}_2\text{O}_3|\text{Fe}) = 3.5 \text{ J/m}^2$ ]. We  
28 note that the  $\text{Fe}_2\text{O}_3$  does not significantly segregate to the surface despite the fact that its  
29 surface energy is smaller than that of  $\text{Cr}_2\text{O}_3$ , but tends to form a strong  $\text{Fe}_2\text{O}_3|\text{Fe}$  interface.  
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38 **Stainless steel buffer at the alumina|zinc interface.** The spatial distribution of com-  
39 ponents in a stainless steel buffer introduced at the alumina|zinc interface under the same  
40 three oxidizing conditions is shown in Fig. 4. With respect to the previous description, the  
41 main modifications take place at the interfaces with Zn and alumina, while the distribution  
42 of components in the core of the buffer remains nearly unchanged.  
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47 Under oxygen-lean conditions, Fig. 4 (top), a segregation of Fe takes place at the inter-  
48 face with  $\text{Al}_2\text{O}_3$ , while Fe and Ni move to the interface with Zn. The resulting component  
49 sequence is  $\text{Al}_2\text{O}_3|\text{Fe}|\text{Fe,Cr,Ni,Zn}|\text{Fe,Ni}|\text{Zn}$ . Driven by its excess in the buffer, Fe segregates  
50 at the contact with  $\text{Al}_2\text{O}_3$ , as it does at the surface of a self-standing buffer. At the Zn  
51 interface, the enrichment in Ni is due to a favorable alloying thermodynamics between these  
52 two metals. Thanks to the presence of the stainless steel buffer, Zn avoids a direct contact  
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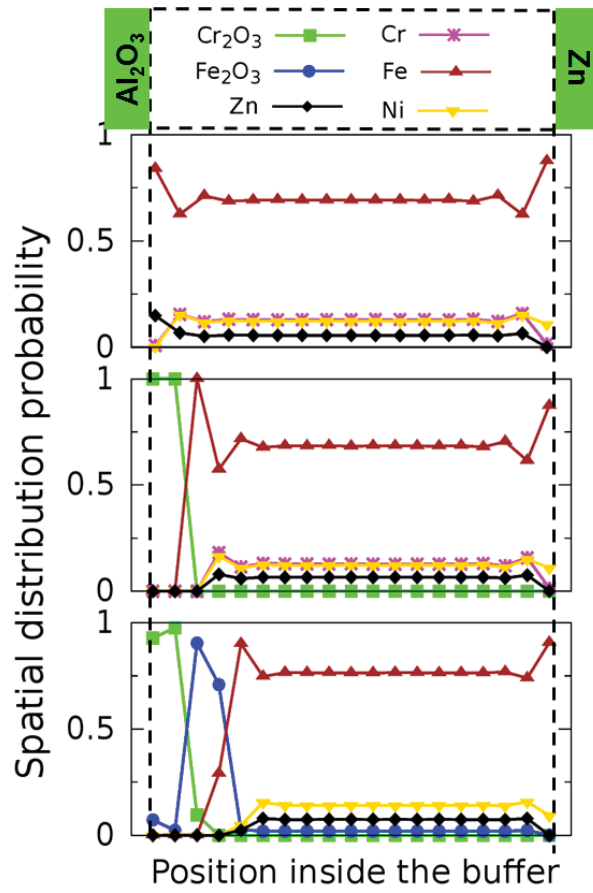


Figure 4: Same as Figure 3 for a buffer sandwiched between alumina and zinc.



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7 with the  $\text{Al}_2\text{O}_3$  substrate, which strengthens the system. In order to quantify the effect, the  
8 distribution of the individual interfaces formed within the buffer, ordered by their adhesion  
9 energy, is given in Fig. 5 (pink line). The least adhesive interface under oxygen-lean en-  
10 vironment is the  $\text{Al}_2\text{O}_3|\text{Fe}$  one, with an adhesion energy of about  $1.9 \text{ J/m}^2$ , which is much  
11 larger than that of  $\text{Al}_2\text{O}_3|\text{Zn}$  ( $0.65 \text{ J/m}^2$ ). It is also larger than the adhesion at the  $\text{Zn}|\text{Zn}$   
12 interface ( $1.06 \text{ J/m}^2$ ), which is representative for the strength of the anti-corrosive coating  
13 itself.  
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20 Under oxygen-moderate conditions, Fig. 4 (middle),  $\text{Cr}_2\text{O}_3$  tends to segregate at the in-  
21 terface with alumina, without a noticeable impact on the remaining buffer sequence  $\text{Al}_2\text{O}_3|\text{Cr}_2\text{O}_3|\text{Fe}|\text{Fe,Cr,N}$   
22 The weakest interfaces become the  $\text{Cr}_2\text{O}_3|\text{Fe}$  and  $\text{Fe}|\text{Zn}$  ones, with an adhesion energy of  
23 about  $3.0 \text{ J/m}^2$ , Fig. 5 (green line), larger than that obtained for the fully metallic buffer.  
24 Further oxidation of the stainless buffer, Fig. 4 (bottom), adds the  $\text{Fe}_2\text{O}_3$  component, which  
25 is found to mainly segregate at the oxide|metal interface. The buffer sequence thus be-  
26 comes  $\text{Al}_2\text{O}_3|\text{Cr}_2\text{O}_3|\text{Fe}_2\text{O}_3|\text{Fe}|\text{Fe,Fe}_2\text{O}_3,\text{Cr,Ni,Zn}|\text{Fe,Ni}|\text{Zn}$ . Owing to a good adhesion at the  
27  $\text{Fe}_2\text{O}_3|\text{Fe}$  contact, the weakest interface is the  $\text{Fe}|\text{Zn}$  one, with an adhesion energy close to  
28  $3.0 \text{ J/m}^2$ , Fig.5 (blue line). Under such oxygen-rich conditions, some of the iron oxide also  
29 appears in the central part of the buffer, due to the low  $\text{Fe}_2\text{O}_3|\text{Fe}$  interface energy.  
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40 Under oxidizing conditions, the separation of oxide and metal components in the buffer  
41 is driven by small interface energies of the oxide|oxide interfaces and negative  $E_{\text{int}}$  of the  
42 metal|metal ones, as compared to large positive  $E_{\text{int}}$  found for metal|oxide contacts. Inter-  
43 estingly, the segregation of Fe to the metal/oxide interfaces whether the interface energetics  
44 is favorable ( $\text{Fe}_2\text{O}_3|\text{Fe}$  and  $\text{Cr}_2\text{O}_3|\text{Fe}$ ) or not ( $\text{Al}_2\text{O}_3|\text{Fe}$ ) is mainly due to iron excess in the  
45 stainless steel buffer.  
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52 Accordingly, let us stress that the buffer characteristics are relatively insensitive to the  
53 precise values of  $E_{\text{int}}$  and  $W$ . On the one hand, the separation of oxide and metal compo-  
54 nents is driven by the fact that most  $E_{\text{int}}$  (oxide|metal) are much larger than oxide|oxide and  
55 metal|metal interface energies. Beyond the computational accuracy, this difference of inter-  
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face energies is due to the very different nature of metal|metal, oxide|oxide, and metal|oxide interfaces. On the other hand, Fe excess in the stainless steel buffer rather than precise interface energy values is responsible for the Fe segregation at metal|oxide interfaces and for the suppression of weakly adhesive zinc|oxide contacts. Thus, our conclusions should not be altered by either a different choice of the exchange-correlation functional, or by refinements in the structural description of the interfaces.

In summary, our results show that stainless steel buffers, when fully metallic, substantially improve the strength of alumina|zinc junctions, by replacing this particularly weak oxide|metal interface by a much more adhesive alumina|iron one. Interestingly, a (partial) oxidation of the buffer, associated with the formation of chromium and/or iron oxides, does not degrade the good buffer performance. This is assigned to a clear separation of all oxide and metallic components (i.e., to the reduction of the number of thermodynamically less stable oxide|metal interfaces), and to the segregation of Fe towards the oxide|metal interface (i.e., suppression of any Zn|oxide interface). When increasing the oxidizing conditions, these effects move the weakest individual interface from alumina|iron to chromia|iron and (metal|metal) Fe|Zn interfaces.

## Discussion

We have developed a simplified model which accounts for the interactions which take place when a multi-component stainless steel buffer is introduced between an alumina substrate and a zinc coating. The comparison with the case of a single-component buffer which follows shows that the adhesion performance under realistic oxidizing conditions is greatly improved. We will then analyze how these performances are modified by either atom inter-diffusion at the interface or by a change of the Cr/Fe or Ni/Fe concentration ratios in the stainless steel.

**Comparison between single- and multi-component buffers.** We have shown in the past that, while single-component metallic buffers improve substantially the adhesion at an

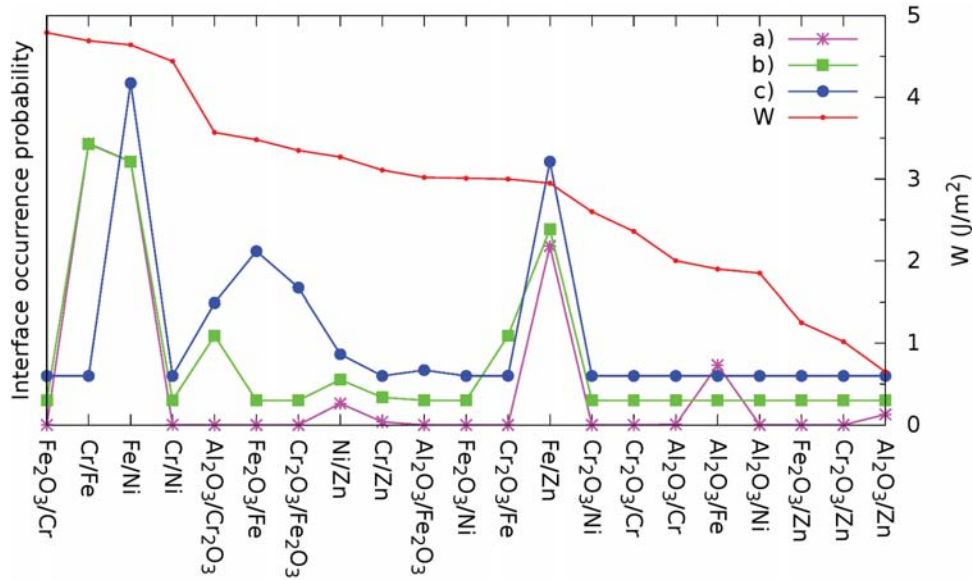


Figure 5: Distribution of individual interfaces in stainless steel buffers with respect to their adhesion energy in the three oxidizing environments: oxygen-lean (a), oxygen-moderate (b) and oxygen-rich (c), and their corresponding adhesion energies (red line, right-hand side scale). For clarity, (b) and (c) diagrams have been vertically shifted with respect to (a).

alumina|zinc interface, their oxidation has a strong detrimental effect due to the weakness of either alumina|oxide or oxide|zinc interfaces.<sup>23</sup> The present results show that, at variance, multi-component buffers are much less subject to such deficiencies, thanks to their selective oxidation and to a favorable component separation. On the one hand, any weak oxide|zinc interface is efficiently replaced by much more adhesive oxide|Fe ones, owing to a strong thermodynamic tendency for iron segregation at the oxide|metal interfaces. On the other hand, the presence of transition metal oxides which result from the partial buffer oxidation and their segregation towards the alumina substrate efficiently suppress the somewhat weaker alumina|metal interfaces. As a consequence, with respect to a well-performing purely metallic buffer (oxygen-lean conditions), the partial buffer oxidation (oxygen-moderate and oxygen-rich conditions), which is unavoidable under realistic oxidizing environments, tends to additionally improve the performance of a multi-component buffer, while it drastically reduces that of a single-component one.

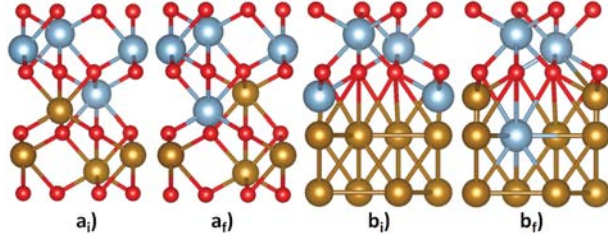


Figure 6: Initial (*i*) and final (*f*) configurations representing a cationic exchange at oxide|oxide (a) and oxide|metal (b) interfaces.

**Inter-diffusion at oxide|oxide and oxide|metal interfaces.** At temperatures typical for the galvanic fabrication of anti-corrosive coatings, an inter-diffusion of atoms at the interfaces may occur. Such possibility was neglected in our *ab initio* simulations of individual interfaces, Sec. 3, but metal mixing was taken into account in an effective way by the Monte Carlo procedure.

We now mimic inter-diffusion effects by exchanging interfacial cations at oxide|oxide and oxide|metal interfaces, Fig. 6. With the help of DFT calculations, we estimate the associated modifications of interface and adhesion energies. We have verified that in all cases the exchange of interface ions is more favorable than that of bulk ones, which makes it the most likely to occur at finite temperatures. The results are summarized in Tab. 4.

The changes of interface energy  $\Delta E_{\text{int}}$  due to a cationic exchange at oxide|oxide interfaces are relatively small, suggesting that such exchanges may occur under realistic conditions. The small values of  $\Delta E_{\text{int}}$  are assigned to the fact that the exchanges preserve the cation oxidation state as well as the number and type of metal-oxygen bonds. Most importantly, the ionic exchange does not substantially downgrade the interface adhesion at the  $\text{Cr}_2\text{O}_3|\text{Fe}_2\text{O}_3$  interface, while it noticeably increases it at the  $\text{Al}_2\text{O}_3|\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3|\text{Fe}_2\text{O}_3$  interfaces. As a whole, adhesion energies remain large at all oxide|oxide interfaces under consideration.

In the case of alumina|metal interfaces, a cationic exchange systematically provokes an increase of interface energy, which becomes more and more important along the series  $M = \text{Cr, Fe, and Ni}$ . The explanatory argument is in line with that already developed for interface energies, Sec. 3. Indeed, in the present case, strong Al-O bonds connecting the terminal

**Table 4: Change of interface  $\Delta E_{\text{int}}$  ( $\text{J}/\text{m}^2$ ) and adhesion  $\Delta W$  ( $\text{J}/\text{m}^2$ ) energies due to a cationic exchange at oxide|oxide and oxide|metal interfaces, and resulting adhesion  $W'$  and interface  $E'_{\text{int}}$  energies ( $\text{J}/\text{m}^2$ ).**

Interface	$\Delta E_{\text{int}}$	$\Delta W$	$E'_{\text{int}}$	$W'$
$\text{Al}_2\text{O}_3 \text{Cr}_2\text{O}_3$	0.01	0.42	0.39	3.99
$\text{Al}_2\text{O}_3 \text{Fe}_2\text{O}_3$	0.27	0.90	0.70	3.92
$\text{Cr}_2\text{O}_3 \text{Fe}_2\text{O}_3$	0.32	-0.16	0.49	3.19
$\text{Al}_2\text{O}_3 \text{Cr}$	0.84	0.52	2.85	2.52
$\text{Al}_2\text{O}_3 \text{Fe}$	1.43	0.88	3.59	2.78
$\text{Al}_2\text{O}_3 \text{Ni}$	1.81	1.91	3.91	3.76
$\text{Cr}_2\text{O}_3 \text{Fe}$	0.18	0.65	1.31	3.65
$\text{Cr}_2\text{O}_3 \text{Ni}$	0.89	0.71	2.31	3.31
$\text{Fe}_2\text{O}_3 \text{Cr}$	-0.49	-0.58	-1.70	4.21
$\text{Fe}_2\text{O}_3 \text{Ni}$	0.30	-0.03	0.81	2.98

alumina cation are replaced by weaker bonds, the strength of which decreases progressively along the series. While this unfavorable energetics suggests that such ionic exchanges will be thermodynamically prohibited under realistic conditions, it is important to point out that, in any case, they would not reduce the interface strength. We find only a small  $\Delta W$  for  $\text{Al}_2\text{O}_3|\text{Cr}$  and  $\text{Al}_2\text{O}_3|\text{Fe}$ , but a substantial increase of adhesion at the  $\text{Al}_2\text{O}_3|\text{Ni}$  interface.

The energetics of cationic exchange at transition metal oxide|metal interfaces can be rationalized with the same arguments, but it is associated with systematically smaller  $\Delta E_{\text{int}}$ , because the Cr-O and Fe-O bonds are weaker than the Al-O ones. In the case of  $\text{Cr}_2\text{O}_3|\text{metal}$  interfaces, the trend when passing from Fe to Ni is the same as before and mixing induces a noticeable increase of adhesion. Small modifications of interface and adhesion energies are obtained at the  $\text{Fe}_2\text{O}_3|\text{Ni}$  interface. The peculiarity of the  $\text{Fe}_2\text{O}_3|\text{Cr}$  interface is the negative value of  $\Delta E_{\text{int}}$ , driven by the instability of this interface, already noted in Sec. 3.

Let us note that if an inter-diffusion occurs at the interfaces, it does not alter the hierarchy of the key interface energies, which is responsible for the separation of metal and oxide components in the buffer. Indeed, interface energies of metal|oxide interfaces remain much

larger compared to those of oxide|oxide and metal|metal ones. Also, the segregation of iron to the oxide interfaces, which is due principally to its excess in the buffer, should not be affected by cation mixing at the interfaces. Finally, the adhesion energies, even if somewhat modified by the inter-diffusion, remain in all cases much larger than those of the reference  $\text{Al}_2\text{O}_3|\text{Zn}$  and  $\text{Zn}|\text{Zn}$  interfaces.

In summary, cation inter-diffusion at oxide|oxide and at some oxide|metal interfaces may be expected under realistic conditions, but it will not substantially modify the buffer structure and will not degrade the buffer performance.

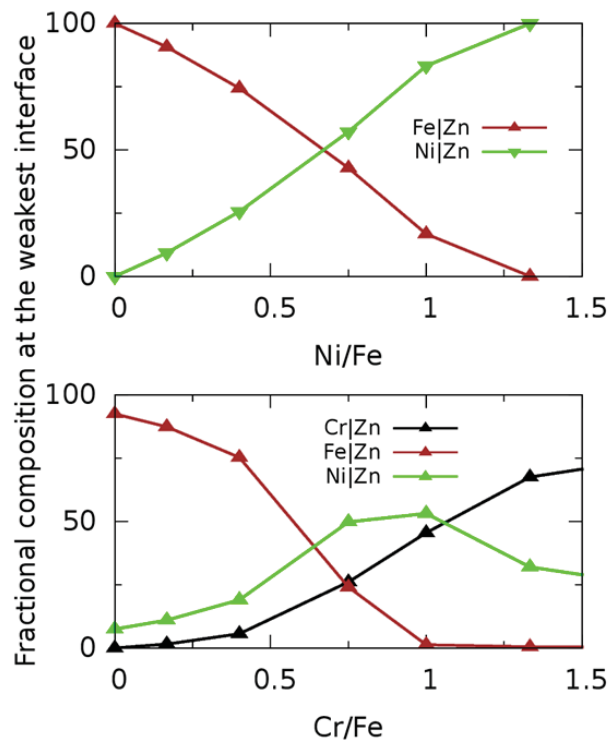


Figure 7: Consequences of a change of buffer composition: (a) proportion of Fe|Zn and Ni|Zn interfaces as a function of the Ni/Fe concentration ratio (oxygen-rich conditions); and (b) proportion of Cr|Zn, Ni|Zn, and Fe|Zn interfaces as a function of the Cr/Fe concentration ratio (oxygen-moderate conditions).

**Modification of stainless steel composition.** In order to estimate how the performance of the stainless steel buffer may be modified by a change of composition, we now consider a progressive increase of the Ni/Fe or Cr/Fe concentration ratios.

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Whatever the oxygen conditions, an increase of the Ni content is found to mainly affect the composition of the contact between stainless steel and the zinc coating. At low Ni concentrations the contact is Fe-rich, but Fe becomes progressively replaced by Ni as the concentration of the latter increases. Such an enrichment of the junction in Ni is thermodynamically favored by the more negative interface energy of the Ni|Zn interface, Tab. 2. Fig. 7 (top) illustrates this effect in the case of oxygen-rich conditions. Interestingly, since  $W(\text{Ni}|\text{Zn}) > W(\text{Fe}|\text{Zn})$ , Tab. 2, the Ni-enrichment is predicted to additionally improve the adhesion of the zinc coating to the stainless steel buffer.

When changing the Cr/Fe concentration ratio, the metal|zinc contact progressively switches from Fe|Zn to Ni|Zn and Cr|Zn. Fig. 7 (bottom) illustrates this effect in the case of oxygen-moderate conditions. An increase of adhesion of about 0.2-0.3 J/m<sup>2</sup> results, Tab. 2. However, since  $W(\text{Ni}|\text{Zn}) > W(\text{Cr}|\text{Zn})$ , an excessive enrichment in Cr may be not optimal for the buffer performance.

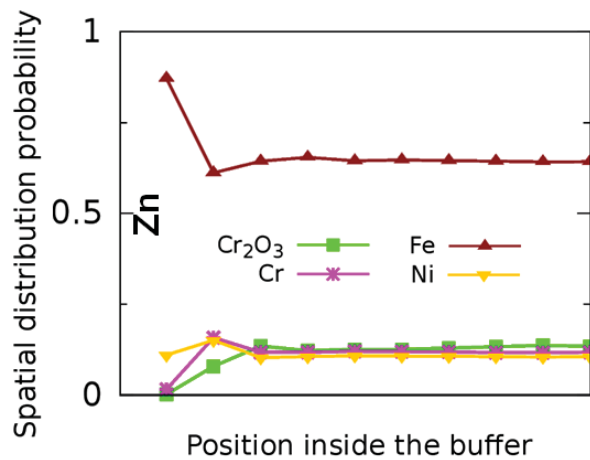


Figure 8: Spatial distribution of components in the stainless steel buffer coated with zinc under oxygen-moderate oxidizing conditions.

Before concluding, it is worth pointing out the two main limitations of our present multi-component buffer model. On the one hand, we have assumed that the buffer structure may be represented by a stacking of perfect two-dimensional layers. In that way, we transformed the complex three-dimensional buffer structure into a one dimensional stack of components.

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6 This enabled a significant reduction of the structural complexity and made its optimiza-  
7 tion computationally treatable. However, in realistic buffers, the various components (e.g.,  
8 oxides) may form finite size crystallites terminated by facets of different orientations. We  
9 note however that, by assuming a layer geometry, our present model tends to over-estimate  
10 the detrimental role of the individual weak (and high energy) interfaces. For example, the  
11 presence of finite size oxide crystallites embedded in a metal matrix instead of an infinite  
12 oxide film is expected to reduce the contribution of weak metal|oxide interfaces to the overall  
13 buffer strength.  
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22 On the other hand, our study is based on thermodynamic considerations only and the  
23 effects driven by the kinetics of ion diffusion are neglected. We note that while the high  
24 temperature of the hot-dip galvanization may reduce to some extent the possibility of kinetic  
25 hindrance, an extension aiming at an explicit account for ion diffusion is necessary for a sound  
26 description of buffer oxidation at ambient temperatures. For example, we find that a strong  
27 thermodynamic bias makes chromia segregate at the alumina interface, while, under the  
28 actual fabrication conditions, the consecutive deposition of the stainless steel buffer and  
29 of the zinc coating may result in the formation of a protective chromia film on the buffer  
30 surface before zinc is deposited. To get some insight into its consequences, we have modeled  
31 an isolated buffer|zinc system under moderate oxidizing conditions, Fig. 8. We find that,  
32 despite the presence of chromia, the contact with the zinc coating is composed uniquely of  
33 Fe and Ni, similarly to the results discussed in Sec. 4. The effect is driven by the high  
34  $\text{Cr}_2\text{O}_3|\text{Zn}$  interface energy and shows that even if chromia component cannot, for kinetic  
35 reasons, entirely segregate at the alumina surface, the Fe and Ni components will efficiently  
36 eliminate it from the buffer|zinc junction.  
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## Conclusions

In summary, relying on DFT calculations of the energetic characteristics of individual interfaces, we have investigated how the presence of a multi-component buffer impacts the adhesion characteristics at a weak alumina|zinc interface, and we have identified the key factors responsible for its strength. To this goal, interface and adhesion energies of a variety of oxide|oxide, metal|metal, oxide|metal interfaces have been quantified at the *ab initio* level, and rationalized by analyzing the number and type of interfacial metal-oxygen bonds. Thermodynamic equilibrium structures of multi-components buffers under various oxidizing conditions were then determined by a MC Metropolis approach and their least adhesive parts, relevant for the overall system performance, have been identified.

By considering stainless steel buffers composed of iron alloyed with chromium and nickel, we have broadened our earlier predictions which only applied to single-component buffers. We have shown that adhesion is improved thanks to the iron segregation at the oxide|metal interface, resulting in the replacement of the particularly weak alumina|zinc contact by a much more adhesive alumina|iron one. Even more interestingly, we have demonstrated that the formation of chromium and iron oxides, which may be unavoidable under realistic oxidizing conditions, does not degrade the performances of such multi-component buffers. This effect, which contrasts with the predictions made for single-component buffers, is mainly due to the separation of the oxide and metal components.

Additionally, we have shown that tuning the composition of the stainless steel may further improve its performances. Both an increase of the Ni concentration and a moderate increase of Cr concentration may be beneficial to adhesion owing to strong Ni-Zn and Cr-Zn interactions. Besides their direct interest for the optimization of industrial adhesive buffers, our results show that an explicit account for selective oxidation and component segregation in a buffer is necessary for a correct estimation of its adhesion characteristics.

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## References

- (1) Marder, A. R. The Metallurgy of Zinc-Coated Steel. *Prog. Mater. Sci.* **2000**, *45*, 191–271.
- (2) Jiang, H.-T.; Ding, W.; Tang, D.; Huang, W. Mechanical Property and Microstructural Characterization of C-Mn-Al-Si Hot Dip Galvanizing TRIP Steel. *J. Iron and Steel Research* **2012**, *19*, 29–36.
- (3) Nikulin, I.; Sawaguchi, T.; Tsuzaki, K. Effect of Alloying Composition on Low-Cycle Fatigue Properties & Microstructure of Fe-30Mn-(6-x)Si-xAl TRIP/TWIP Alloys. *Materials Science and Engineering A* **2013**, *587*, 192–200.
- (4) Wang, W.; Li, M.; He, C.; Wei, X.; Wang, D.; Dub, H. Experimental Study on High Strain Rate Behavior of High Strength 600-1000 MPa Dual Phase Steels and 1200 MPa Fully Martensitic Steels. *Materials and Design* **2013**, *47*, 510–521.
- (5) Mertens, A.; Bellhouse, E. M.; McDermid, J. R. Microstructure and Mechanical Properties of a Mixed Si-Al TRIP-Assisted Steel Subjected to Continuous Galvanizing Heat Treatments. *Materials Science & Engineering A* **2014**, *608*, 249–257.

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- (6) Drillet, P.; Zermout, Z.; Bouleau, D.; Maigne, J.-M.; Claessens, S. Selective Oxidation of High Si, Mn and Al Steel Grades During Recrystallization Annealing and Steel/Zn Reactivity. *Rev. Metall.-Cah. Inf. Tech.* **2004**, *10*, 831–837.
  - (7) Guttman, M. Diffusive Phase Transformations in Hot Dip Galvanizing. *Materials Science Forum* **1994**, *155-156*, 527–548.
  - (8) Triboulet, R.; Perriere, J. Epitaxial Growth of ZnO Films. *J. Progress in Crystal Growth and Characterization of Materials* **2003**, *47*, 65–138.
  - (9) Campbell, C. T. Ultrathin Metal Films and Particles on Oxide Surfaces: Structural, Electronic and Chemisorptive Properties. *Surface Science Reports* **1997**, *27*, 1–111.
  - (10) Bogicevic, A.; Jennison, D. R. Variations in the Nature of Metal Adsorption on Ultrathin Al<sub>2</sub>O<sub>3</sub> Films. *Phys. Rev. Lett.* **1999**, *82*, 4050–4053.
  - (11) Batyrev, I. G.; Alavi, A.; Finnis, M. W. Equilibrium and Adhesion of Nb/sapphire: The Effect of Oxygen Partial Pressure. *Phys. Rev. B* **2000**, *62*, 4698–4706.
  - (12) Siegel, D. J.; Hector, J. L. G.; Adams, J. B. Adhesion, Atomic Structure, and Bonding at the Al(111)/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) Interface: A First Principles Study. *Phys. Rev. B* **2002**, *65*, 085415.
  - (13) Hernandez, N. C.; Graciani, J.; Márquez, A.; Sanz, J. F. Cu, Ag and Au Atoms Deposited on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) Surface: A Comparative Density Functional Study. *Surf. Sci.* **2005**, *575*, 189–196.
  - (14) Briquet, L. G. V.; Catlow, C. R. A.; French, S. A. Comparison of the Adsorption of Ni, Pd, and Pt on the (0001) Surface of  $\alpha$ -Alumina. *J. Phys. Chem.* **2008**, *112*, 18948–18954.
  - (15) Melnikov, V. V.; Yermeev, S. V.; Kulkova, S. E. Theoretical Investigations of 3d-Metal Adsorption on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) Surface. *Russ. Phys. J.* **2011**, *54*, 704–712.

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- (16) Li, H.; Zhang, W.; Smith, J. R. Advances in ab initio Thermodynamic Studies on Metal/Oxide Interfaces. *Phys. Stat. Solidi A*. **2011**, *208*, 1166–1173.
- (17) Yoshitake, M.; Yagyū, S.; Chikyow, T. Novel Method for the Prediction of an Interface Bonding Species at Alumina/Metal Interfaces. *J. Vac. Sci. Technol. A* **2014**, *32*, 021102-1–8.
- (18) Lazzari, R.; Goniakowski, J.; Cabailh, G.; Cavallotti, R.; Trcera, N.; Lagarde, P.; Jupille, J. Surface and Epitaxial Stresses on Supported Metal Clusters. *Nano Lett.* **2016**, *16*, 2574–2579.
- (19) Rodriguez, J. A.; Kuhn, M.; Hrbek, J. Interaction of Silver, Cesium, and Zinc with Alumina Surfaces: Thermal Desorption and Photoemission Studies Interaction of Silver, Cesium, and Zinc with Alumina Surfaces: Thermal Desorption and Photoemission Studies. *J. Phys. Chem.* **1996**, *100*, 18240–18248.
- (20) Lazzari, R.; Jupille, J.; Cavallotti, R.; Simonsen, I. Model-free Unraveling of Supported Nanoparticles Plasmon Resonance Modes. *J. Phys. Chem. C* **2014**, *118*, 7032–7048.
- (21) Cavallotti, R.; Goniakowski, J.; Lazzari, R.; Jupille, J.; Koltsov, A.; Loison, D. Role of Surface Hydroxyl Groups on Zinc Adsorption Characteristics on Al<sub>2</sub>O<sub>3</sub>(0001) Surfaces: First-Principles Study. *J. Phys. Chem. C* **2014**, *118*, 13578–13589.
- (22) Cavallotti, R.; Le, H.-L. T.; Goniakowski, J.; Lazzari, R.; Jupille, J.; Koltsov, A.; Loison, D. New Routes for Improving Adhesion at Metal/Al<sub>2</sub>O<sub>3</sub>(0001) Interface. *Phys. Chem. Chem. Phys.* **2016**, *18*, 3032–3039.
- (23) Le, H.-L. T.; Goniakowski, J.; Noguera, C.; Koltsov, A.; Mataigne, J.-M. First-Principles Study on the Effect of Pure and Oxidized Transition-Metal Buffers on Adhesion at the Alumina/Zinc Interface. *J. Phys. Chem. C* **2016**, *120*, 9836–9844.

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- (24) Le, H.-L. T.; Lazzari, R.; Goniakowski, J.; Cavallotti, R.; Chenot, S.; Noguera, C.; Jupille, J.; Koltsov, A.; Mataigne, J.-M. Tuning Adhesion at Metal/Oxide Interfaces by Surface Hydroxylation. *J. Phys. Chem. C Letters* **2017**, *121*, 11464–11471.
- (25) Kresse, G.; Furthmuller, J. Efficient Iterative Schemes for ab initio Total Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (26) Kresse, G.; Hafner, J. Ab initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558–561.
- (27) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (28) Kresse, G.; Joubert, J. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (29) Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.* **2004**, *92*, 246401.
- (30) Klimes, J.; Bowler, D. R.; Michaelides, A. Chemical Accuracy for the van der Waals Density Functional. *J. Phys.: Cond. Matt.* **2010**, *22*, 022201.
- (31) Klimes, J.; Bowler, D. R.; Michaelides, A. Van der Waals Density Functionals Applied to Solids. *Phys. Rev. B* **2011**, *83*, 195131.
- (32) Chase, M. W. NIST-JANAF Thermochemical Tables, Fourth Edition. *J. Phys. Chem. Ref. Data* **1998**, *Monograph 9*, 1–1951.
- (33) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: New York, 1984.
- (34) Momma, K.; Izumi, F. VESTA 3 for Three-dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *41*, 1272–1276.

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- (35) Punkkinen, M. P. J.; Hu, Q.-M.; Kwon, S. K.; Johansson, B.; Kollár, J.; Vitos, L. Surface Properties of 3d Transition Metals. *Philosophical Magazine* **2011**, *91*, 3627–3640.
- (36) Ruberto, C.; Yourdshahyan, Y.; Lundqvist, B. I. Surface Properties of Metastable Alumina: A Comparative Study of  $\kappa$ - and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. *Phys. Rev. B* **2003**, *67*, 195412.
- (37) Rohrbach, A.; Hafner, J.; Kresse, G. Ab initio Study of the (0001) Surfaces of Hematite and Chromia: Influence of Strong Electronic Correlations. *Phys. Rev. B* **2004**, *70*, 125426.
- (38) Frenkel, D., Smit, B., Eds. *Understanding Molecular Simulation: From Algorithms to Applications*, 1st ed.; Academic Press, Inc.: Orlando, FL, USA, 1996.

# Graphical TOC Entry

