Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

First-principles atomistic thermodynamics study on the early-stage corrosion of NiCr alloy under fluoride salt environment

Ya-Ru Yin,[ab] **Cui-Lan Ren**,[*ac] **Han Han**,[ad] **Jian-Xing Dai**,[a] **Hao Wang**,[ab] **Ping Huai**,[*ad] **and Zhi-Yuan Zhu**,[ac]

[a] *Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

[c] *Key Laboratory of Interfacial Physics and Technology, Chinese Academy of Sciences, Shanghai 201800, China*

[d] *School of Physical Science and Technology, Shanghai Tech University, Shanghai 201210, China*

***Corresponding author.**

Associate Professor., Ph.D.; Tel: +86 21 33512449; Fax: +86 21 33512449

E-mail address: rencuilan@sinap.ac.cn (Cui-Lan Ren)

Professor., Ph.D., Tel: +86 21 39194793; Fax: +86 21 39194793

E-mail address: huaiping@sinap.ac.cn (Ping Huai)

Table S1. Surface segregation energies (in eV) of Cr at the surface, second, third and "bulk" layers of the Cr-doped Ni (111) surface in 2 ×2 square expansion of the surface cell with the dimensions of 4.978 Å ×4.311 Å, in the absence (E_{segr}^{Cr})/presence ($E_{segr}^{Cr(F)}$) of fluorine adsorption.

Cr position	Cr-doped Ni (111) surface			
	"bulk" layer	3rd layer	2nd layer	surface layer
E_{segr}^{Cr}	0	-0.03	-0.14	0.19
$E_{segr}^{Cr(F)}$	0	-0.04	-0.16	-0.46

Table S2. Gibbs free energies of formation (in KJ/mol) per molecule of F_2 for the salt constituents, hydrogen fluoride and the metal fluorides at 850 ℃, were calculated by HSC Chemistry 6.0 computer software, which are in line with the results of Olson' work.[1]

Gibbs free energy of formation	LiF	NaF	KF	CrF_2	CrF_3	HF	NiF_2	CrF_4
	-1017	-919	-909	-635	-605	-560	-483	-418

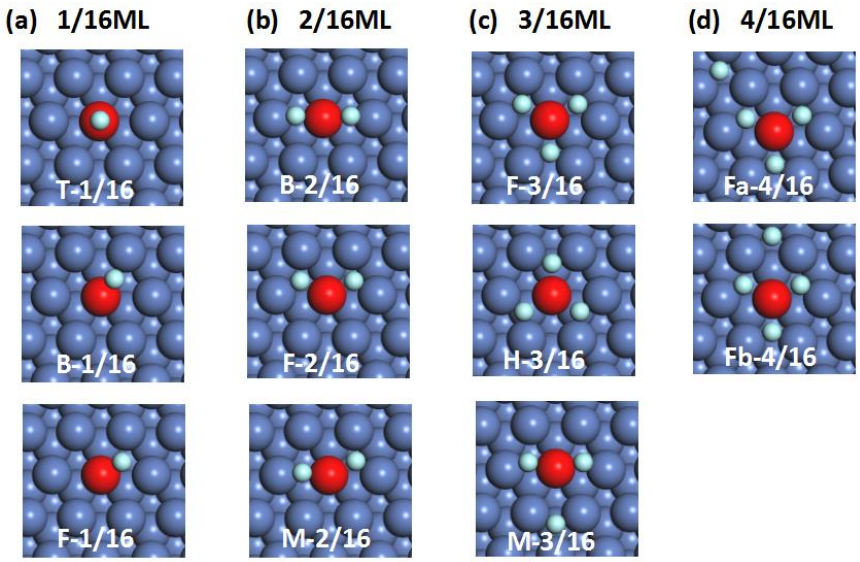

Fig. S1 Top views of on-surface adsorption configurations at different fluorine coverages of (a) 1/16, (b) 2/16, (c) 3/16, and (d) 4/16 ML on Cr-doped Ni (111) surface. Herein, the atomic Ni, Cr, and F atoms are represented by the dark blue, red and green balls, respectively.

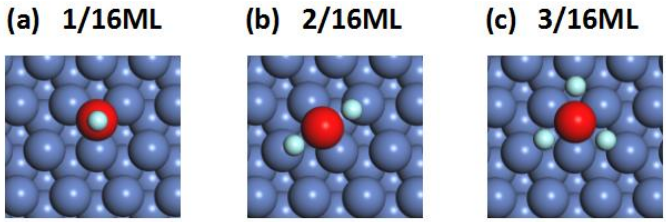

Fig. S2 Top views of fluorine atoms chemisorbed near the Cr adatom on pure Ni (111) surface at different fluorine coverages of (a) 1/16, (b) 2/16, and (c) 3/16 ML.

References

1 L. C. Olson, J. W. Ambrosek, K. Sridharan, M. H. Anderson and T. R. Allen, *J. Fluor. Chem.*, 2009, **130**, 67.